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# Canadian Journal of Technology

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## A RADIAL HEAT FLOW APPARATUS FOR THE DETERMINATION OF THERMAL CONDUCTIVITY[1]


BY A. C. BURR[2]



### Abstract

The apparatus described was designed for routine measurement of the thermal conductivity of materials in the range 0.001 to 0.1 c.g.s. units but could be modified easily for measurements on metals or on refractory materials. The apparatus has proved to be reliable and rugged. It is well suited to routine measurement in that samples can be changed and operation resumed in about an hour's time. Armco Iron was used as a check on the operation of the apparatus since its conductivity is accurately known. Results of determinations on this material between 400°C. and 700°C. are shown, together with results for a typical sample of petroleum coke electrode carbon. The accuracy is estimated to be about ±5%.


### Introduction and Theory

The amount of heat that is conducted per unit time through any cross section of a substance depends upon the temperature gradient at that section and the area of the section. Calling the sectional area $A$, the rate of heat transfer is,

$$q = k\frac{(t_2 - t_1)A}{S},$$

where $k$ = a constant called the thermal conductivity of the substance,*

$t_2 - t_1$ = the temperature difference,

$S$ = the distance over which the temperature difference is measured.

To measure the thermal conductivity of a substance it is necessary to pass heat through it in a known direction and to observe the rate at which heat passes through a given cross section of it under a known temperature gradient.


[1] *Manuscript received June 13, 1951.*
*Contribution from the Divisions of Physics and Physical Metallurgy, Aluminium Laboratories Limited, Kingston, Ont.*



[2] *Physicist, Aluminium Laboratories Limited.*


* *k is actually only a constant for the case where the temperature difference and the distance over which it is measured are incremental, i.e., in the formula*

$$q = kA\frac{dt}{ds}.$$

*In practice, of course, the temperature interval and distance must be large enough to be measured accurately and since for most materials k is a function of temperature the values reported are those for the mean temperature of the temperature interval.*

In testing metals, since their thermal conductivity is relatively high, a method commonly used has been the "Forbes bar" method where specimens are in the form of rods. Heat is supplied at one end, passes longitudinally down the rod, and is extracted at the other end. If the heat input is measured, one has to be certain that all the heat supplied passes into the bar; if the output is measured, that all the heat from the bar passes into the calorimeter. Provision has to be made so that no heat escapes from the bar along its length.

In measuring the thermal conductivity of poor conductors the specimens are often in the form of sheets or slabs up to 1 or 2 in. in thickness so that the heat path will be short and of large sectional area. A long heat path is not necessary since the gradients are relatively large. Otherwise the method of testing is the same as for good conductors.

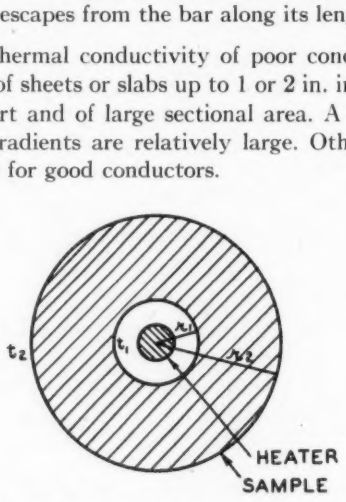


FIG. 1. *Heat conduction through a cylindrical specimen with a central axial hole.*

When a radial heat flow method is used, the heat passes outward through layers of varying area. Fig. 1 represents a cross section through a cylindrical specimen with a central axial hole. The heat conducted through the wall of such a specimen per unit time is given by,

$$q = \frac{2\pi k(t_1 - t_2)}{\ln(r_2/r_1)}$$

from which

$$k = \frac{q \ln(r_2/r_1)}{2\pi(t_1 - t_2)}.$$

When an electrically operated heater is used the quantity $q$ can be obtained from the power supplied to the heater. The thermal conductivity in c.g.s. units will then be given by,

$$k = \frac{IV \ln(r_2/r_1)}{2\pi \times 4.186L(t_1 - t_2)}$$

where $IV/L$ = watts dissipated per unit length of the heater.

The radial heat flow apparatus described below for measuring the thermal conductivity of carbonaceous materials was designed to avoid difficulties encountered with other designs previously tried. In apparatus where the speci-

mens were in the form of rods the driving heater was necessarily small and considerable difficulty was found in getting sufficient heat into the specimen. Contact between sample and calorimeter, or heat sink, was uncertain and guard heaters to prevent radial heat leakage were quite elaborate. Also, no system of locating thermocouples to measure the temperature gradient in the specimen was found that was suitable for apparatus intended for routine measurement.

Apparatus similar to that described in the ASTM Standards (1) for measuring the thermal conductivity of firebrick and other refractory materials was found completely unreliable on materials of medium or high conductivity. The erratic behavior on these materials is due mainly to nonuniformity of thermal contact at the various interfaces in the system, e.g., hot plate to sample and sample to calorimeter. In materials of very low conductivity the difference in heat flow between areas of good and poor contact is so small as to be practically negligible, i.e., the conductivity of the materials themselves is of the same order as that of the interfaces. In addition the low conductivity materials for which high temperature values are needed are nearly all refractory materials which can be measured in an air atmosphere thus reducing the effect of variable interface contact still further.

## Experimental

The radial heat flow apparatus shown schematically in Fig. 2 is designed to avoid interfaces of the type described above. Specimens are in the form of circular cylinders about 6 in. in diameter and $1\frac{3}{4}$ to $2\frac{1}{4}$ in. in length with a central axial hole $1\frac{1}{2}$ in. in diameter. A test assembly is a stack of five such cylinders the center one being the sample under test, the other four being guard cylinders. The stack could be solid but the plane interfaces between cylinders are a help in that they provide some impedance to axial heat flow. The five-piece construction also facilitates boring the thermocouple holes. A standard "hot plate" electric range element is placed in contact with each end of the stack to serve as a guard heater and further assurance against axial heat flow. A long slender heating element placed coaxially in the hole in the test assembly supplies heat to the specimens. A heater made from No. 14 Chromel A wire wound on a helically grooved alundum form 1 in. O. D. with a 1/9-in. groove pitch will heat specimens to 700° or 800°C. For temperatures above 800°C. a $\frac{1}{2}$-in. diameter graphite rod was used as a heating element. A helix of molybdenum wire would probably be better than the graphite rod at the higher temperatures since it would eliminate the difficulties involved in clamping current leads to the brittle, relatively fragile graphite in a manner to preserve good contact continuously from room temperature to operating temperature. The heater is supplied from a welding transformer the windings of which were modified to supply up to 500 amp. continuously at 20 v.

The thermocouples used are made from No. 20 B & S gauge chromel and alumel wire. Couples Nos. 1 and 2 are $1\frac{1}{4}$ in. apart and measure the temperature difference in the sample under test. They are led into this sample along

isotherms and are located on a radius at the mid plane of the central specimen. Couples Nos. 3 and 4 enter the "hot plates" through holes bored on a radius in the heavy cast iron plate. The depth of these holes is such that the thermocouple bead is located at a point whose temperature should be the mean of the temperatures measured by couples Nos. 1 and 2. The "hot plates" are supplied through independent variac transformers so that their temperatures can be

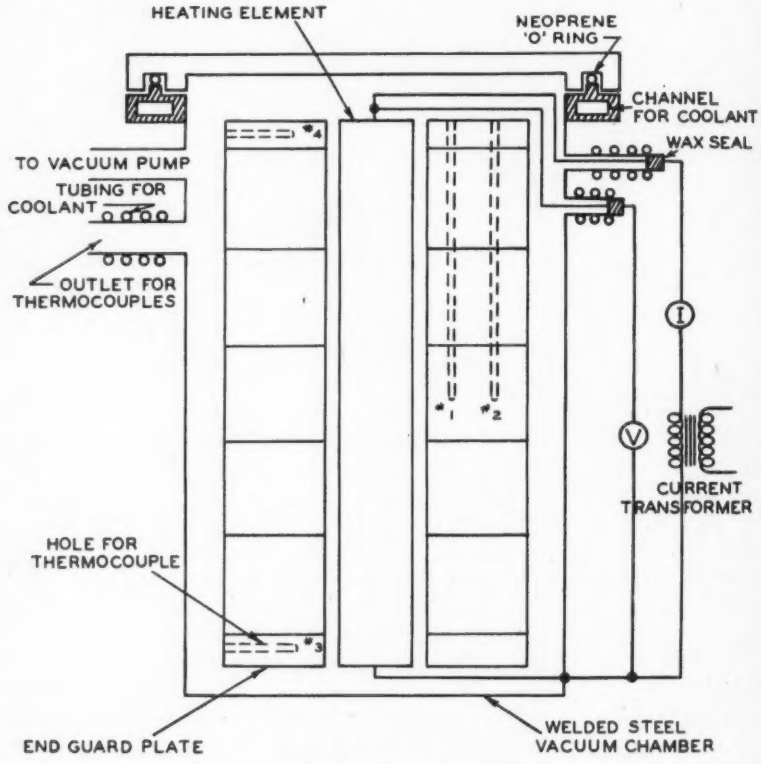


FIG. 2. *Sketch of specimen arrangement.*

regulated. Thermocouples are brought out of the vacuum enclosure through water-cooled wax seals to a double pole rotary switch, so that each couple can be connected in turn to a precision portable potentiometer. Voltage and current supplied to the central heater are read on meters accurate to $\frac{1}{2}\%$ full scale. A rough vacuum is maintained around the test assembly by a megavac rotary type oil pump which is kept running during operation. The pump is connected to the vacuum chamber through 2 in. I.D. piping for rapid pump-down.

The apparatus can be pumped down to operating pressure (0.05 to 0.5 mm.) in about 10 min. Heaters are then turned on and the apparatus allowed to come

to equilibrium at a temperature close to the one chosen. This takes about five hours. As the sample temperature approaches equilibrium the end heaters are adjusted so that their monitor couples are within one or two degrees of the mean sample temperature. When equilibrium is reached readings are taken at half hour intervals until five or six values of $k$ are obtained and these are averaged for the $k$ value at that mean equilibrium temperature. When the apparatus has cooled sufficiently specimens can be changed and operation resumed in about an hour's time.

## Results

In Table I and Fig. 3 are shown some typical results obtained on Armco Iron using this radial heat flow apparatus. Also shown are the results of Armstrong and Dauphinee (2) and Powell (3).

TABLE I

| Armco Iron (Armstrong and Dauphinee) | | Armco Iron (Powell) | | Armco Iron (Author) | | Petroleum coke (Author) | |
|---|---|---|---|---|---|---|---|
| Temp.,°C. | $k$, c.g.s. units | Temp.,°C. | $k$, c.g.s. units | Temp.,°C. | $k$, c.g.s. units | Temp.,°C. | $k$, c.g.s. units |
| 0 | 0.182 | 0 | 0.177 | | | | |
| 100 | 0.166 | 100 | 0.163 | | | 104 | 0.0049 |
| 200 | 0.149 | 200 | 0.147 | | | 217 | 0.0056 |
| 300 | 0.133 | 300 | 0.132 | | | 318 | 0.0061 |
| 400 | 0.118 | 400 | 0.116 | 445 | 0.109 | 403 | 0.0064 |
| 500 | 0.106 | 500 | 0.103$_5$ | 510 | 0.106 | 516 | 0.0067 |
| 600 | 0.094 | 600 | 0.093 | 611 | 0.093 | 626 | 0.0070 |
| 700 | 0.082 | 700 | 0.062 | 735 | 0.079 | 723 | 0.0073 |
| | | | | | | 834 | 0.0076 |

Thermal conductivity values obtained for petroleum coke electrode samples are given in Table I and illustrated graphically in Fig. 4. Samples of both iron and carbon were in sets of five, each sample being approximately $2\frac{1}{4}$ in. thick and 6 in. in diameter with a central hole $1\frac{1}{2}$ in. in diameter.

## Discussion

The radial heat flow apparatus has proved to be reliable and rugged. It is also fairly well suited to routine measurement. From our ability to reproduce experimental values and our measurements on Armco Iron the accuracy is estimated to be about $\pm 5\%$ for the materials measured to date. It should be realized, however, that this apparatus was designed primarily for measurements on materials whose conductivity is of the same order as that of carbonaceous materials. It is not, in its present form, well suited to measurements on metals as the heat path is too short thus making the temperature interval too small to measure accurately. This is particularly true at the lower temperatures

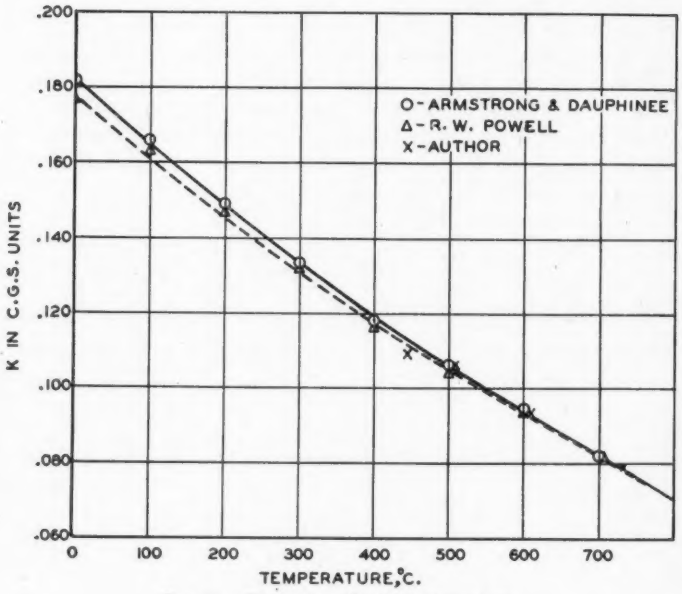


FIG. 3. *Thermal conductivity Armco iron.*

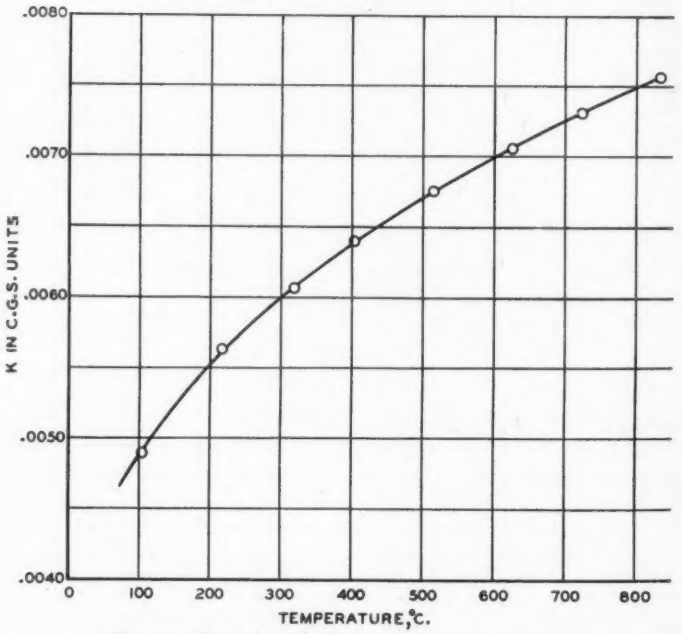


FIG. 4. *Thermal conductivity petroleum coke carbon.*

(below 450°C.) where the temperature difference in Armco Iron samples is less than five degrees. For measurements on metals a larger vacuum chamber should be used so that samples of greater diameter could be accommodated. For materials of low conductivity samples of smaller diameter may be used or thermocouple spacing reduced.

If accuracy better than 5% is required it can be obtained, at the expense of operating convenience, by using thermocouples of smaller wire and improving the guards against axial heat flow. This can be done either by adding additional guard specimens or by sectionalizing the guard heater windings so that the radial gradient in the heater approximates the radial gradient in the test specimen. Further improvement could probably be obtained by making taps on the axial heater and measuring voltage drop across only that portion of it inside the test specimen.

The original design of this apparatus used a graphite rod $\frac{1}{2}$ in. in diameter as a central heater. This type of heating element requires a large current at low voltage but considerably higher temperatures can be reached with it than with the chromel heater. Graphite is, however, very brittle and the current clamps necessary for the large currents need careful attention. For this reason a change was made to the wire wound heating element. If temperatures higher than 800° or 900°C. are desired molybdenum wire could be substituted for chromel wire in the heater.

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# CANADIAN WILTSHIRE BACON

## XXXI. EFFECTS OF SALT CONTENT AND STORAGE TEMPERATURE ON STORAGE LIFE[1]

By N. E. Gibbons, Dyson Rose, and J. W. Hopkins


### Abstract

Assessment of the quality of pork and bacon after storage at temperatures from 10° to 40°F. showed that the optimum temperature for storage of wrapped, Wiltshire type bacon was 20° to 23°F. At higher temperatures bacteria developed on the lean meat and caused spoilage; at lower temperatures development of oxidative rancidity in the fat was accelerated. Above 23°F. unsalted pork spoiled more rapidly than bacon, but below this temperature the storage life of pork exceeded that of bacon quite markedly. Varying the salt content of bacon from 2% to 6% had only a moderate effect on storage life at any of the experimental temperatures; at 30°F. each additional 1% salt prolonged the storage time three to four days on the average.


### Introduction

One of the chief complaints against Canadian Wiltshire bacon has been its excessive saltiness (18). A previous investigation (10) indicated that a salt content of 3.5 to 4.0% in the lean meat was preferred by a panel of Canadian consumers but this level is frequently exceeded in an attempt to improve the keeping quality of the product. Further investigations have also shown that Wiltshire-cured bacon increases in apparent saltiness during storage (6).

While it is generally recognized that a high salt content prolongs the storage life of meat products, especially when refrigeration is inadequate, no extensive study of the interrelations between salt content, storage temperature, and keeping quality is available. Callow (1) has shown that, after three and one-half months' storage at 32° and 27°F., bacon was tainted; at 19° or 14°F. the flavor was poor or moderately good, while at 5° or −13°F. the product remained in excellent condition. In a later experiment (2) in which the bacon was frozen at −22°F. and then stored at 14°F., the lean remained in excellent condition for five months, but the fat lost its antioxidant properties in two months. The salt content of this bacon is not recorded. The work of Lea (12) on bacon, and more recently that of Wiesman and Ziemba (17) and of Watts and Peng (15) on sausage meat has shown that sodium chloride accelerates the development of rancidity in fat held at low temperatures. Few additional data on the storage life of bacon can be found in the literature, though considerable work has been done with frozen pork (e.g. 8, 11, 14). The present work was therefore undertaken to study quantitatively the storage life of bacon over a range of temperatures and salt contents.

[1] *Manuscript received July 24, 1951.*
*Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada; final paper of the "Canadian Wiltshire Bacon" series. Issued as Paper No. 267 of the Canadian Committee on Food Preservation and as N.R.C. No. 2533.*

## Materials and Methods

Two experiments were undertaken, the first at temperatures of 10°, 20°, 30°, and 40°F., the second at 20°, 23°, 27°, and 30°F. With only minor exceptions, the same methods and procedures were used throughout.

For each experiment, 104 fresh, rib-in export backs were halved and the halves assigned at random to one of the specified combinations of salt content, storage temperature, and storage period. Uncured (pork) samples were wrapped in wax paper, overwrapped in Kraft, and placed in storage. Curing was effected in the laboratory by pumping, followed by curing in pickle for two or three days. All pickles contained 1.0% sodium nitrate and 0.05% sodium nitrite, but the extent of pumping, duration of cure, and sodium chloride content of the pump and cover pickles were varied to produce three levels (approximately 3, 4, and 5%) of saltiness. After cure the samples were drained for 24 hr., then wrapped as described above, and stored.

Single half backs were withdrawn at intervals of from 4 to 15 days depending on the storage temperature. After sampling the surface for bacterial counts, the half backs were trimmed, boned, and sliced. One of each pair of successive 3 mm. slices was then randomly selected for tasting, and the other was ground to provide material for chemical analysis. Organoleptic appraisals were made immediately; material for chemical analysis was stored at −40°F. until sampled.

*Bacteriological*

Surface samples of 3 sq. cm. were outlined with stainless steel cutters and removed with sterile scalpels and forceps. Four such disks were taken from each sample during Experiment I, and 20 disks during Experiment II. These disks were shaken in 100 ml. of 4% sodium chloride with quartz chips, diluted appropriately, and plated in agar containing 0.5% Difco proteose–peptone, 0.5% Difco tryptone, and 4% salt. The plates were incubated at 70°F. and bacterial counts were made after four days.

*Chemical*

Chloride, nitrate, and nitrite were determined on aliquots of a hot water extract of ground lean meat; chloride by titration with silver nitrate using potassium chromate as the indicator (16), nitrate by a modified brucine method (13), and nitrite by the sulphanilic acid – α-naphthylamine reaction (16). Moisture was estimated by determining the weight lost during drying at 221°F. for 15 hr.

For fat extraction, approximately 20 gm. of fatty tissue was placed in a 150 ml. beaker and covered with a watch glass fitted loosely within the beaker. The beaker was heated on a steam bath for 20 min., and the watch glass was pressed down with a glass rod from time to time to facilitate the melting. The liquid fat was then squeezed from under the watch glass and drained into a warm 15 ml. centrifuge tube. This liquid was centrifuged for five minutes at 1500

r.p.m., and aliquots of the tissue-free supernatant fat were measured into flasks and weighed for analysis.

Free fatty acid was determined by titration in an ethanol–toluene solution, peroxide oxygen by iodimetric titration in a glacial acetic acid – chloroform solution, and α-dicarbonyl by color formation during heating in the presence of ethanol and potassium hydroxide (7).

*Subjective Appraisal*

For taste panel appraisal, slices were broiled at approximately 500°F. for three minutes on one side and for one minute on the other, and served hot. A maximum of four appraisals twice daily was required of the panel, and the order of presentation of the sample slices, which were identified only by code numbers, was randomly permuted. The taste panels for Experiments I and II consisted of 22 and 23 members respectively. Tasters made and recorded their judgments independently in a partitioned appraisal laboratory in which standard temperature, humidity, ventilation, and lighting were maintained (9). In Experiment I, appraisals were quantified (10) by a scoring scale on which the integers from −5 through zero to +5 were assigned to 11 defined gradations of flavor intensity as follows:

| | |
|---|---|
| Gross excess | +5 |
| Very decided excess | +4 |
| Decided excess | +3 |
| Moderate excess | +2 |
| Slight excess | +1 |
| Ideal | 0 |
| Slight deficiency | −1 |
| Moderate deficiency | −2 |
| Decided deficiency | −3 |
| Very decided deficiency | −4 |
| Gross deficiency | −5 |

In Experiment II, only the upper six points of the scale were used to score appraised intensities of strong and undesirable flavors.

*Statistical*

Statistical analysis made of the surface bacterial counts and of the flavor scores recorded in Experiments I and II comprised the following steps. (i). Graduation of the sequence of observations $y_t$ on half backs of the same salt category successively withdrawn from storage at any one temperature by an unweighted least-squares polynomial regression function of time

$$y_t = b_0 + b_1t^2 + \ldots\ldots\ldots\ldots + b_nt^n$$

of the degree, mostly the third or fourth, required to stabilize the residual variance $s^2y$ (4, Sec. 29) of the experimental $y_t$ from the graduated $Y_t$. (This residual variance was not significantly reduced by inclusion of the salt con-

tent reported for individual half backs as an additional independent variate.) (ii). Determination from each such regression equation of the time at which the graduated surface bacterial count and average flavor score first attained $10^7$ per cm.$^2$ and $+1.5$ respectively, the former being adopted as the average slime point (5) and the latter as the point at which about two-thirds of individuals would detect some degree of undesirable flavor, individual scores being distributed about the average for each sample with a standard deviation of rather more than one scale unit. (iii). Relation of these calculated times, regarded as indices of storage life for comparative purposes, to the imposed storage conditions. The estimated error variance $s_t^2$ of these last estimates was computed to a first order approximation (3, Sec. 62) from the relation

$$s_t^2 = s_y^2 \left[ \sum_{i=0}^{i=n} \sum_{j=0}^{j=n} c_{ij} \frac{(\partial t)}{(\partial b_i)} \frac{(\partial t)}{(\partial b_j)} \right]$$

in which the $c_{ij} = \Delta_{ij}/\Delta$ are the ratios of the minors $\Delta_{ij}$ to the determinant $\Delta$ of the numerical coefficients of the regression parameters $b_0, b_1, \ldots\ldots\ldots, b_n$ in the $(n + 1)$ normal equations specifying these latter. These determinantal ratios were evaluated by the inverse matrix procedure systematized by Fisher (4, Sec. 29).

## Results

*Chloride, Nitrate, and Nitrite Contents*

Sodium chloride concentrations actually found by analysis of samples from individual half backs varied appreciably. In Experiment I the ranges for the three cures were from 1.3 to 4%, from 2.7 to 5.1%, and from 3.2 to 6.6%, with averages of 2.7, 4.0, and 4.8% respectively. In Experiment II the corresponding ranges were 1.4 to 3.8%, 2.6 to 6.2%, and 3.2 to 7.0%, with averages of 2.8, 4.3, and 5.5%. For convenience, the different cures will therefore be referred to below as "3", "4", and "5"% salt respectively.

In Experiment I the average concentrations of nitrate at the beginning of storage were 0.03, 0.14, and 0.13% for the 3, 4, and 5% salt cures respectively, and this constituent showed no significant variation with time of storage at the temperatures used. The average concentrations of nitrite for the three cures were 22, 52, and 31 p.p.m. respectively 24 hr. after cure. During storage at 40 and 30°F. the nitrite content increased somewhat but showed considerable variation from sample to sample. At 20° and 10°F. no trend with storage time was apparent.

In Experiment II the average nitrate contents for the three cures at the beginning of storage were 0.13, 0.14, and 0.20% respectively and again no significant variation was noted with time. The average levels of nitrite were 26, 28, and 31 p.p.m. respectively and these increased during storage at a rate roughly proportional to the temperature throughout the 10-degree range studied. The increase recorded at 20°F. was very small and possibly not significant.

*Development of Rancidity*

In the uncured (pork) samples, rancidity developed chiefly as a result of hydrolytic processes, as shown by an increased free fatty acid content in the extracted fat. Rancidity developed relatively rapidly in samples stored at 40°

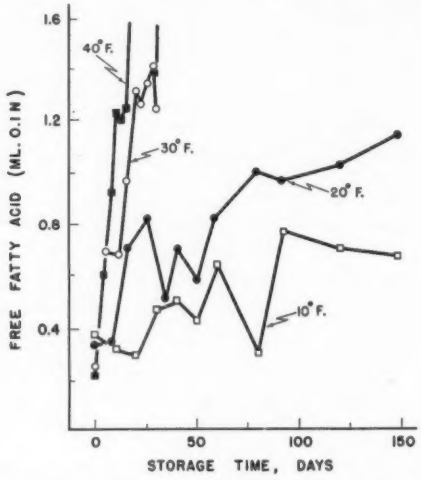


FIG. 1. *Effect of temperature on the development of free fatty acids in fatty tissue of pork (Expt. I).*

and 30°F. but more slowly in frozen samples stored at 20° and 10°F. (Fig. 1). Similarly, in the second experiment the accumulation of free fatty acids was more or less proportional to the temperature of storage.

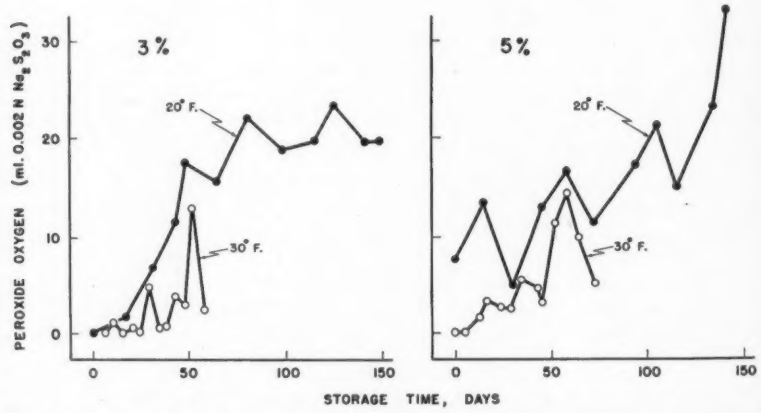


FIG. 2. *Effect of temperature and salt concentration on development of oxidative rancidity in fatty tissue of bacon (Expt. II).*

In the bacon samples the development of rancidity was primarily due to oxidation, although the free fatty acid content of the fat increased to some extent during storage. Unfortunately, the analyses of the fat from the first experiment were not made until the samples had been stored some time at −40°F. and since even at this temperature further oxidative changes had occurred in the ground material, these data are not reported. The peroxide values for the 3% and 5% salt cures in Experiment II are presented in Fig. 2; the 4% cure behaved similarly. Decreasing the storage temperature did not prevent but actually accelerated development of oxidative rancidity as determined by peroxide oxygen values. The concentration of salt in the bacon had no significant over-all effect on the peroxide oxygen values. The α-dicarbonyl values showed the same general trends as the peroxide oxygen and are not reported.

*Bacterial Numbers*

The logarithm of the count per sq. cm. of lean meat surface of all samples is given in Appendix Tables A and B. In Experiment I (Appendix Table A) the bacterial count rarely reached the specified slime level (log 7.0/sq. cm.) at temperatures of 20° and 10°F. However at 30° and 40°F. this level was reached fairly quickly and the salt content of the bacon had very little influence on bacterial growth.

Logarithms of the bacterial counts obtained in the second experiment are also plotted in Fig. 3, but the counts on meat stored at 27°F. have been omitted since they overlapped those at 30° and 23°F. At 20°F. all samples were frozen hard and bacterial growth was very slow. At 27°F., on the other hand, none

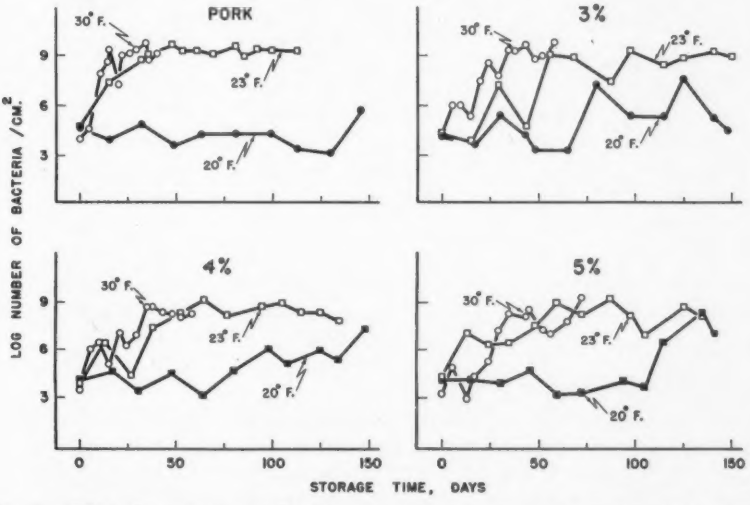


FIG. 3. *Effect of temperature and salt concentration on growth of surface bacteria on pork (0% salt) and bacon (3, 4, and 5% salt) (Expt. II).*

of the samples was frozen and bacterial growth was fairly rapid. At 23°F. most of the 3% salt samples were frozen hard and growth was slow, but the 4% and 5% samples were not frozen and growth was quite rapid.

*Subjective Appraisal Scores*

The average flavor scores given to the samples in Experiment I are shown in Appendix Table A; those given to the samples of the second experiment are shown in Appendix Table B. Some of the results obtained in Experiment II are illustrated in Fig. 4.

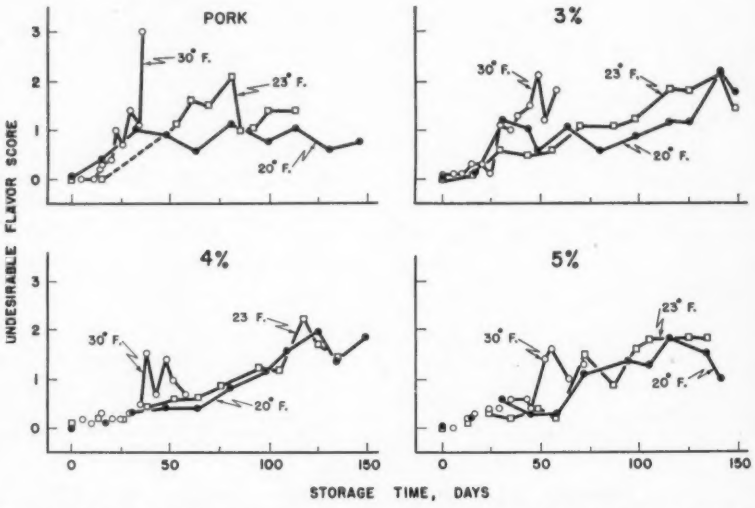


FIG. 4. *Effect of temperature and salt concentration on rate of development of undesirable flavors in pork (0% salt) and bacon (3, 4, and 5% salt) (Expt. II).*

In both experiments the pork rapidly attained a panel average flavor score of 1.5 at temperatures of 23°F. and above, but at 10° and 20°F. this score was barely attained during the entire storage period. On the other hand, the bacon developed undesirable flavor less rapidly than pork at the higher temperatures but more rapidly at the lower. Increasing the salt content of the meat from 3 to 5% prolonged the storage life slightly at the higher temperatures but had an adverse effect at 20°F. At the lower temperatures the development of off-flavors was largely due to the formation of rancid flavor in the fat.

*Calculated Storage Life*

Text Table I shows the calculated storage life, deduced as described, of the meat under all test conditions prior to the attainment of a surface bacterial count of $10^7$ per sq. cm. and of an average score for undesirable flavor intensity of 1.5 units. Salt contents listed in this table are the actual averages obtained on analysis rather than the 3, 4, and 5% salt cure designations used for con-

venience in the preceding paragraphs. At the higher temperatures both the bacterial counts and the flavor scores changed rapidly and the uncertainty of estimation of storage life was consequently relatively small. At the lower storage temperatures on the other hand changes were slow and storage life

TABLE I

EFFECT OF STORAGE TEMPERATURE AND SALT CONTENT OF BACON ON THE TIME REQUIRED TO DEVELOP A SPECIFIED SURFACE BACTERIAL COUNT AND OFF-FLAVOR SCORE

| Expt. No. and storage temp., °F. | Average salt content, % | Estimated number of days to attainment of: | |
|---|---|---|---|
| | | Bacterial count of $10^7$/cm.$^2$ | Flavor intensity score of +1.5 |
| I. 10° | 0.0 | >160 | >160 |
| | 2.5 | >160 | 97 ± 10 |
| | 3.8 | >160 | 97 ± 7 |
| | 4.4 | >160 | 105 ± 10 |
| I. 20° | 0.0 | >160 | 176 ± 11 |
| | 2.8 | >160 | 119 ± 11 |
| | 3.8 | 142 ± 22 | 116 ± 8 |
| | 4.6 | 132 ± 11 | 111 ± 11 |
| II. 20° | 0.0 | >160 | >160 |
| | 2.8 | >160 | 129 ± 8 |
| | 3.9 | >160 | 119 ± 5 |
| | 5.1 | 132 ± 6 | 116 ± 9 |
| II. 23° | 0.0 | 16 ± 5 | 84 ± 10 |
| | 2.9 | 45 ± 11 | 105 ± 6 |
| | 4.6 | 37 ± 9 | 108 ± 8 |
| | 5.9 | 32 ± 8 | 107 ± 7 |
| II. 27° | 0.0 | 11 ± 3 | 77 ± 8 |
| | 3.0 | 17 ± 4 | 85 ± 4 |
| | 4.5 | 25 ± 6 | 84 ± 3 |
| | 5.7 | 50 ± 9 | 93 ± 4 |
| I. 30° | 0.0 | 7 ± 3 | 32 ± 2 |
| | 2.7 | 10 ± 4 | 41 ± 2 |
| | 4.3 | 13 ± 4 | 49 ± 5 |
| | 5.4 | 16 ± 4 | 47 ± 6 |
| II. 30° | 0.0 | 9 ± 3 | 32 ± 2 |
| | 2.7 | 20 ± 3 | 41 ± 3 |
| | 4.0 | 29 ± 5 | 39 ± 2 |
| | 5.3 | 31 ± 3 | 57 ± 3 |
| I. 40° | 0.0 | 4 ± 2 | 17 ± 2 |
| | 2.8 | 4 ± 2 | 25 ± 2 |
| | 4.2 | 6 ± 2 | 34 ± 2 |
| | 4.9 | 9 ± 2 | 38 ± 3 |

could be estimated, if at all, only with a low degree of precision, nine of the bacterial count and two of the flavor score regression functions failing to attain log $10^7$ and 1.5 respectively even when extrapolated to 180 days.

Storage lives at 10° and 20°F. deduced from the bacterial index were generally somewhat longer than those resulting from the flavor index, but at 23°F.

and higher temperatures this differential was markedly reversed. The flavor index storage lives obtained at the two temperatures included in both experiments, namely 20° and 30°F., were in reasonable agreement, none of the seven determinate discrepancies exceeding 1.9 times its estimated standard error. However, the average bacterial index storage life of bacon stored at 30°F. was significantly shorter in Experiment I.

In Table II the storage life of pork is contrasted with that of bacon (unweighted averages of all salt contents). In frozen storage at 20°F. the storage

TABLE II

EFFECT OF STORAGE TEMPERATURE ON THE TIME REQUIRED TO DEVELOP A SPECIFIED SURFACE BACTERIAL COUNT AND OFF-FLAVOR SCORE IN PORK AND BACON

| Expt. No. and storage temp., °F. | Estimated number of days to attainment of: | | | |
|---|---|---|---|---|
| | Bacterial count of $10^7$/cm.$^2$ | | Flavor intensity score of +1.5 | |
| | Pork | Bacon* | Pork | Bacon* |
| I. 10° | >160 | >160 | >160 | 100 ± 5 |
| I. 20° | >160 | 145 ± 8 | 176 ± 11 | 115 ± 6 |
| II. 20° | >160 | 151 ± 6 | >160 | 121 ± 4 |
| II. 23° | 16 ± 5 | 38 ± 6 | 84 ± 10 | 107 ± 4 |
| II. 27° | 11 ± 3 | 31 ± 4 | 77 ± 8 | 87 ± 3 |
| I. 30° | 7 ± 3 | 13 ± 3 | 32 ± 2 | 46 ± 3 |
| II. 30° | 9 ± 3 | 27 ± 2 | 32 ± 2 | 46 ± 2 |
| I. 40° | 4 ± 3 | 6 ± 2 | 17 ± 2 | 32 ± 2 |

* *Averaged over all salt contents.*

life of the pork exceeded that of the bacon, but the rate of deterioration of the pork was accelerated very greatly as the temperature was increased above 20°F. The storage life of bacon deduced from the bacterial index was at least double that of pork at all temperatures between 23° and 30°F., but was only slightly

TABLE III

ESTIMATED AVERAGE INCREASE PER 1% SALT OVER THE RANGE 2–6% IN THE TIME REQUIRED TO DEVELOP A SPECIFIED BACTERIAL COUNT AND OFF-FLAVOR SCORE

| Expt. No. and storage temp., °F. | Average increment, per 1% additional salt in estimated days to attainment of: | |
|---|---|---|
| | Bacterial count of $10^7$/cm.$^2$ | Flavor intensity score of +1.5 |
| I. 10° | Indet. | +4 ±6 |
| I. 20° | <0 | −4 ±8 |
| II. 20° | <0 | −6 ±5 |
| II. 23° | −4 ±4 | +1 ±3 |
| II. 27° | +12 ±3 | +3 ±2 |
| I. 30° | +2 ±2 | +2 ±2 |
| II. 30° | +4 ±2 | +6 ±2 |
| I. 40° | +2 −1 | +6 ±2 |

longer than that of pork at 40°F. at which temperature bacteria multiplied rapidly on the surface of both types of meat. The difference between pork and bacon respecting flavor deterioration was less marked, but except at 27°F., exceeded twice its estimated standard error.

In Table III the effect of salt (over the range 2 to 6%) on the storage life of bacon is indicated in terms of average increment in calculated storage life per 1% increase in salt content. These results indicate that additional salt increased the storage life (bacterial limit) appreciably at 27°F., and slightly at 30° and 40°, but that the increment in storage life (flavor limit) was indistinguishable from experimental variability at 10°, 20°, 23°, and 27°F., and was only four-six days per additional 1% salt at 30° and 40°F.

## Discussion

From the foregoing test conditions and criteria, the indications were: (i) that maintenance of bacon containing 3-4% salt in good condition for three to four months required a storage temperature not higher than 23°F., and 20°F. was preferable; even at the latter temperature, although sliming was effectively retarded, an objectionable degree of rancidity developed in about 120 days: (ii) that the effect of increasing the salt content up to 6% was generally relatively slight and, even in the vicinity of 27°F., would be hardly enough to justify salt contents in excess of those preferred by consumers: (iii) that at storage temperatures of 23°F. and higher, sliming preceded tainting; thus at 27°F. bacon containing 4.5% salt was stored for an estimated $84 \pm 3$ days before developing a panel average flavor score of +1.5, but had a surface bacterial count of $10^7$ per cm.$^2$ in an estimated $25 \pm 6$ days, and thereafter would not have been marketable without extensive washing and trimming.

In practice, storage life will vary with circumstances. For example the appearance of slime will depend on the numbers and species of organisms initially present on the surface, as well as on the salt content and storage temperature. Then again commercial tolerances for sliminess and taint may, as a result of local conditions, be greater or less than those specified by the indices adopted in this test, the indications from which should therefore be interpreted accordingly. Bacon is seldom condemned because of bacterial slime alone, but in normal marketing this condition may result in considerable wastage from extensive trimming and in severe financial penalties.

## Acknowledgments

Mr. G. A. Grant, now associated with the Defence Research Board, Ottawa, made many of the chemical analyses in the first experiment.

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## APPENDIX TABLE A

THE SURFACE BACTERIAL COUNT (LOG NO. OF BACTERIA PER SQ. CM.) AND THE FLAVOR SCORE OF PORK AND OF BACON CONTAINING 3, 4, AND 5% SALT AFTER STORAGE AT TEMPERATURES OF 10, 20, 30, AND 40°F.

| Temp. | No salt (pork) | | | 3% salt | | | 4% salt | | | 5% salt | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time, days | Bacteria, log no. cm.² | Flavor score | Time, days | Bacteria, log no. cm.² | Flavor score | Time, days | Bacteria, log no. cm.² | Flavor score | Time, days | Bacteria, log no. cm.² | Flavor score |
| 10° | 0 | 3.36 | −0.14 | 0 | 3.77 | −0.59 | 0 | 3.98 | 0.05 | 0 | 3.40 | −0.32 |
| | 11 | 4.41 | −0.14 | 10 | 6.14 | −0.23 | 10 | 4.28 | −0.23 | 10 | 4.94 | −0.23 |
| | 20 | 4.78 | 0.18 | 21 | 6.10 | 0.18 | 21 | 6.42 | 0.14 | 21 | 5.97 | 0.55 |
| | 30 | 4.29 | 0.45 | 30 | 6.76 | 0.45 | 30 | 5.59 | 0.18 | 30 | 5.41 | 0.50 |
| | 40 | 5.31 | 0.41 | 39 | 4.71 | 0.68 | 39 | 4.34 | 0.27 | 39 | 5.89 | 0.59 |
| | 50 | 4.82 | 0.64 | 49 | 5.73 | 1.18 | 49 | 4.68 | 0.73 | 49 | 5.04 | 0.45 |
| | 60 | 4.56 | 1.00 | 59 | 5.70 | 0.64 | 64 | 3.88 | 0.50 | 59 | 5.02 | 0.59 |
| | 81 | 3.66 | 0.77 | 70 | 6.11 | 1.00 | 74 | 6.45 | 1.23 | 79 | 4.95 | 1.41 |
| | 92 | 5.27 | 0.55 | 107 | 4.88 | 2.23 | 87 | 3.54 | 1.68 | 101 | 3.43 | 1.09 |
| | 120 | 5.38 | 0.82 | | | | 107 | 4.75 | 1.55 | 121 | 5.20 | 1.59 |
| | 148 | 4.99 | 0.64 | | | | 127 | 4.82 | 2.22 | 132 | 4.32 | 2.26 |
| | 176 | 4.14 | 1.50 | | | | 136 | 3.37 | 1.78 | | | |
| | 204 | 3.40 | 1.40 | | | | | | | | | |
| 20° | 0 | 4.07 | −0.36 | 0 | 3.55 | −0.64 | 0 | 6.04 | −0.32 | 0 | 4.52 | −0.14 |
| | 8 | 5.46 | −0.73 | 8 | 6.48 | −0.23 | 8 | 5.58 | −0.32 | 8 | 5.83 | −0.27 |
| | 16 | 3.40 | −0.23 | 16 | 6.90 | −0.09 | 16 | 5.34 | −0.09 | 16 | 6.29 | −0.41 |
| | 26 | 5.03 | −0.41 | 24 | 6.95 | 0.45 | 24 | 3.92 | 0.09 | 24 | 5.02 | 0.50 |
| | 34 | 3.52 | 0.68 | 32 | 6.15 | 0.77 | 32 | 5.66 | 0.41 | 32 | 4.22 | 0.50 |
| | 40 | 5.08 | 0.64 | 41 | 4.76 | 0.68 | 41 | 4.46 | 0.41 | 41 | 3.82 | 0.64 |
| | 50 | 4.03 | 0.82 | 49 | 4.49 | 0.64 | 49 | 4.81 | 0.36 | 49 | 3.98 | 1.13 |
| | 58 | 4.68 | 0.41 | 57 | 5.19 | 0.91 | 59 | 5.90 | 0.91 | 57 | 5.92 | 0.86 |
| | 78 | 5.14 | 0.82 | 73 | 5.39 | 1.09 | 79 | 5.55 | 1.23 | 64 | 4.53 | 0.68 |
| | 92 | 4.41 | 0.55 | 87 | 6.26 | 1.55 | 101 | 7.34 | 1.18 | 79 | 4.16 | 1.41 |
| | 120 | 5.23 | 0.82 | 107 | 5.21 | 0.91 | 121 | 5.53 | 1.50 | 101 | 5.38 | 1.18 |
| | 148 | 5.62 | 1.22 | 127 | 5.60 | 1.72 | 132 | 7.28 | 2.18 | 121 | 8.14 | 1.73 |
| | 176 | 5.79 | 1.64 | | | | | | | 132 | 5.62 | 1.94 |
| 30° | 0 | 5.28 | −0.36 | 0 | 4.44 | −0.68 | 0 | 3.87 | −0.50 | 0 | 5.54 | 0.27 |
| | 6 | 5.73 | −0.77 | 6 | 5.61 | −0.32 | 6 | 6.27 | −0.36 | 6 | 4.29 | −0.36 |
| | 12 | 8.77 | −0.18 | 13 | 8.99 | −0.23 | 13 | 8.46 | −0.36 | 13 | 7.17 | 0.05 |
| | 16 | 8.88 | −0.27 | 17 | 9.68 | 0.05 | 17 | 7.42 | 0.09 | 17 | 7.50 | −0.32 |
| | 20 | 5.46 | 0.41 | 21 | 7.52 | 0.14 | 21 | 8.78 | −0.09 | 23 | 6.89 | 0.41 |
| | 22 | 8.62 | 0.45 | 25 | 9.05 | 0.77 | 27 | 9.48 | 0.95 | 29 | 9.81 | 0.64 |
| | 26 | 8.81 | 1.27 | 29 | 8.56 | 0.73 | 31 | 7.78 | 0.41 | 35 | 7.78 | 1.09 |
| | 28 | 9.42 | 1.27 | 31 | 8.10 | 1.41 | 35 | 7.93 | 1.27 | 41 | 9.55 | 0.91 |
| | 30 | 8.61 | 1.95 | 34 | 8.32 | 0.86 | 37 | 8.40 | 0.82 | 45 | 7.23 | 1.55 |
| | 32 | 9.60 | 1.45 | 37 | 8.40 | 0.86 | 41 | 9.60 | 0.68 | 49 | 8.37 | 1.68 |
| | 34 | 9.36 | 1.73 | 41 | 9.67 | 0.68 | 43 | 9 75 | 1.27 | 53 | 7.66 | 1.73 |
| | 36 | 8.79 | 2.36 | 43 | 8.82 | 1.55 | 46 | 8.48 | 2.32 | 57 | 8.74 | 2.09 |
| | | | | 46 | 9.29 | 1.73 | | | | 66 | 9.16 | 1.95 |
| 40° | 0 | 5.52 | −0.41 | 0 | 5.10 | −0.59 | 0 | 5.69 | −0.18 | 0 | 3.82 | −0.18 |
| | 4 | 6.61 | −0.23 | 3 | 7.45 | −0.45 | 3 | 6.75 | 0.05 | 3 | 7.36 | −0.14 |
| | 8 | 9.30 | −0.55 | 8 | 8.13 | −0.18 | 8 | 7.66 | −0.36 | 8 | 5.73 | 0.09 |
| | 11 | 8.51 | 0.14 | 13 | 9.53 | 0.36 | 13 | 8.22 | 0.18 | 13 | 7.96 | −0.05 |
| | 13 | 9.46 | −0.05 | 16 | 9.73 | −0.05 | 16 | 8.39 | 0.18 | 16 | 9.00 | 0.05 |
| | 15 | 8.68 | 0.36 | 18 | 7.29 | 0.86 | 18 | 8.45 | 0.59 | 18 | 7.94 | 0.27 |
| | 18 | 8.76 | 4.14 | 21 | 9.35 | 0.91 | 21 | 7.72 | 0.59 | 23 | 9.13 | 0.45 |
| | 20 | 7.99 | | 24 | 8.22 | 1.55 | 25 | 10.84 | 0.95 | 28 | 9.71 | 0.86 |
| | 22 | 8.61 | | 27 | 9.31 | 1.18 | 29 | 8.96 | 1.68 | 34 | 8.27 | 1.05 |
| | | | | 30 | 8.15 | 1.95 | 31 | 9.48 | 1.73 | 39 | 8.94 | 2.09 |
| | | | | 34 | 8.79 | 2.45 | 34 | 8.83 | 1.50 | 43 | 8.82 | 1.73 |
| | | | | 36 | 8.28 | | 37 | 8.26 | 2.36 | 46 | 8.36 | 2.05 |
| | | | | | | | 41 | 9.28 | 1.64 | | | |

## APPENDIX TABLE B

THE SURFACE BACTERIAL COUNT (LOG NO. OF BACTERIA PER SQ. CM.) AND THE FLAVOR SCORE OF PORK AND BACON CONTAINING 3, 4, AND 5% SALT AFTER STORAGE AT 20, 23, 27, AND 30°F.

| Temp. | No salt (pork) | | | 3% salt | | | 4% salt | | | 5% salt | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time, days | Bacteria, log no./cm.² | Flavor score | Time, days | Bacteria, log no./cm.² | Flavor score | Time, days | Bacteria, log no./cm.² | Flavor score | Time, days | Bacteria, log no./cm.² | Flavor score |
| 20° | 0 | 4.39 | 0.04 | 0 | 4.24 | 0.04 | 0 | 4.01 | 0 | 0 | 3.07 | 0.04 |
| | 15 | 3.44 | 0.40 | 17 | 3.72 | 0.12 | 17 | 4.54 | 0.12 | 15 | 4.12 | 0.20 |
| | 32 | 4.77 | 1.04 | 31 | 5.43 | 1.20 | 31 | 3.43 | 0.32 | 31 | 3.86 | 0.60 |
| | 48 | 3.12 | 0.88 | 43 | 4.24 | 1.04 | 48 | 4.48 | 0.44 | 45 | 4.65 | 0.28 |
| | 63 | 4.33 | 0.56 | 48 | 3.35 | 0.56 | 64 | 3.15 | 0.44 | 58 | 3.22 | 0.28 |
| | 81 | 4.36 | 1.24 | 64 | 3.27 | 1.08 | 80 | 4.61 | 0.84 | 72 | 3.30 | 1.12 |
| | 99 | 4.43 | 0.72 | 80 | 7.27 | 0.56 | 98 | 6.04 | 1.16 | 94 | 3.98 | 1.36 |
| | 113 | 3.20 | 1.04 | 98 | 5.38 | 0.88 | 108 | 5.06 | 1.56 | 105 | 3.69 | 1.28 |
| | 130 | 3.28 | 0.60 | 115 | 5.36 | 1.16 | 125 | 5.99 | 1.96 | 115 | 6.51 | 1.80 |
| | 146 | 5.81 | 0.76 | 125 | 7.64 | 1.16 | 134 | 5.46 | 1.36 | 134 | 8.37 | 1.52 |
| | 153 | 5.01 | 0.80 | 141 | 5.27 | 2.16 | 148 | 7.29 | 1.84 | 141 | 7.15 | 1.00 |
| | 160 | 4.22 | 0.56 | 148 | 4.55 | 1.76 | 155 | 4.22 | 1.68 | 155 | 4.22 | 1.20 |
| 23° | 0 | 5.71 | 0 | 0 | 4.42 | 0 | 0 | 3.86 | 0.12 | 0 | 4.20 | 0 |
| | 15 | 6.83 | 0 | 15 | 3.89 | 0.08 | 13 | 6.42 | 0.20 | 13 | 7.10 | 0.12 |
| | 32 | 9.58 | 2.24 | 29 | 7.24 | 0.56 | 27 | 4.33 | 0.24 | 24 | 6.28 | 0.28 |
| | 36 | 8.94 | 1.88 | 43 | 4.77 | 0.48 | 38 | 7.44 | 0.44 | 35 | 6.46 | 0.20 |
| | 48 | 9.47 | 1.92 | 56 | 9.14 | 0.56 | 52 | 8.38 | 0.60 | 48 | 7.58 | 0.40 |
| | 53 | 9.03 | 1.08 | 69 | 8.90 | 1.08 | 64 | 9.18 | 0.64 | 58 | 9.02 | 0.20 |
| | 61 | 8.83 | 1.60 | 87 | 7.43 | 1.08 | 76 | 8.21 | 0.88 | 72 | 8.34 | 1.48 |
| | 69 | 9.01 | 1.52 | 98 | 9.24 | 1.24 | 94 | 8.84 | 1.24 | 87 | 9.23 | 0.88 |
| | 81 | 9.58 | 2.08 | 115 | 8.39 | 1.84 | 105 | 8.96 | 1.16 | 98 | 8.21 | 1.60 |
| | 85 | 8.73 | 0.96 | 125 | 8.87 | 1.80 | 115 | 8.38 | 2.24 | 105 | 6.96 | 1.76 |
| | 92 | 9.15 | 1.04 | 141 | 9.25 | 2.16 | 125 | 8.39 | 1.68 | 125 | 8.78 | 1.84 |
| | 99 | 9.33 | 1.36 | 148 | 8.92 | 1.44 | 134 | 7.86 | 1.44 | 134 | 8.21 | 1.80 |
| | 113 | 9.05 | 1.36 | | | | 155 | 8.83 | 2.28 | | | |
| 27° | 0 | 3.84 | 0.04 | 0 | 3.94 | 0 | 0 | 4.38 | 0 | 0 | 3.41 | 0.04 |
| | 15 | 7.46 | 0.24 | 9 | 4.11 | 0.16 | 9 | 5.20 | 0.08 | 9 | 2.82 | 0.08 |
| | 29 | 9.03 | 1.12 | 17 | 7.73 | 0.04 | 17 | 7.32 | 0.04 | 17 | 4.78 | 0.08 |
| | 34 | 8.50 | 0.84 | 27 | 9.05 | 0.72 | 27 | 5.93 | 0.40 | 27 | 5.16 | 0.28 |
| | 43 | 9.35 | 0.84 | 35 | 9.42 | 0.24 | 35 | 7.89 | 0.40 | 35 | 6.19 | 0.32 |
| | 50 | 8.19 | 1.40 | 45 | 7.72 | 0.20 | 45 | 8.52 | 0.20 | 45 | 7.55 | 0.36 |
| | 51 | 8.34 | 0.76 | 56 | 8.10 | 0.48 | 56 | 8.71 | 0.32 | 56 | 6.88 | 0.56 |
| | 63 | 8.57 | 1.52 | 64 | 9.22 | 1.04 | 64 | 9.36 | 0.72 | 64 | 6.96 | 0.44 |
| | 74 | 9.40 | 1.56 | 72 | 9.47 | 1.36 | 72 | 8.48 | 1.08 | 72 | 8.76 | 1.52 |
| | 81 | 8.47 | 1.08 | 87 | 8.49 | 1.16 | 87 | 8.86 | 1.60 | 87 | 8.38 | 0.72 |
| | 92 | 8.89 | 1.12 | 94 | 9.65 | 1.76 | 94 | 7.50 | 1.24 | 94 | 8.20 | 1.76 |
| | 99 | 9.04 | 1.44 | 101 | 9.49 | 2.52 | 105 | 9.26 | 2.48 | 101 | 9.19 | 1.88 |
| | 113 | 9.14 | 1.68 | | | | | | | | | |
| 30° | 0 | 3.69 | 0 | 0 | 4.20 | 0.08 | 0 | 3.51 | 0 | 0 | 3.26 | 0 |
| | 4 | 4.58 | 0 | 6 | 6.05 | 0.08 | 6 | 6.08 | 0.16 | 6 | 4.82 | 0 |
| | 11 | 7.53 | 0 | 10 | 6.10 | 0.08 | 10 | 6.49 | 0.08 | 13 | 2.96 | 0.20 |
| | 14 | 8.39 | 0.20 | 15 | 5.38 | 0.28 | 15 | 5.00 | 0.28 | 17 | 4.32 | 0.28 |
| | 15 | 9.58 | 0.30 | 21 | 7.49 | 0.28 | 21 | 7.18 | 0.20 | 24 | 5.27 | 0.40 |
| | 20 | 6.22 | 0.40 | 24 | 8.61 | 0.08 | 24 | 6.24 | 0.16 | 29 | 7.22 | 0.40 |
| | 22 | 8.98 | 0.96 | 29 | 7.77 | 1.08 | 29 | 6.95 | 0.32 | 35 | 8.30 | 0.64 |
| | 26 | 8.94 | 0.68 | 35 | 9.38 | 1.04 | 35 | 8.78 | 0.52 | 43 | 8.21 | 0.64 |
| | 29 | 9.30 | 1.36 | 38 | 9.32 | 1.32 | 38 | 8.85 | 1.52 | 45 | 8.65 | 0.44 |
| | 34 | 9.19 | 1.08 | 43 | 9.71 | 1.48 | 43 | 8.45 | 0.68 | 52 | 7.30 | 1.40 |
| | 36 | 8.61 | 2.96 | 48 | 8.75 | 2.12 | 48 | 8.31 | 1.36 | 56 | 7.12 | 1.72 |
| | 40 | 9.06 | | 52 | 8.94 | 1.24 | 52 | 8.80 | 0.96 | 64 | 7.86 | 1.04 |
| | | | | 58 | 9.80 | 1.76 | 58 | 8.31 | 0.68 | 72 | 9.25 | 1.36 |

# A STUDY ON THE POSSIBLE PRODUCTION OF GLYCEROL FROM SULPHITE WASTE LIQUOR BY YEAST[1]

By Diarmuid Murphy[2]

## Abstract

Samples of yeast grown on treated sulphite waste liquor in the presence of added sulphites produced ethanol and glycerol in still- and shake-cultures; consumption of sugar was low and yields of glycerol were small. The addition of sulphites to the medium slowed the fermentation. Attempts to acclimatize the yeast to the medium, or variation in the amounts of added nitrogen or phosphorous compounds, did not improve the rate of fermentation, sugar utilization, or glycerol production. Increasing the sugar content of the medium with sugar-beet molasses yielded no improvement. It was concluded that sulphite waste liquor was not a suitable medium for this fermentation.

## Introduction

The production of glycerol by yeasts has been long known, Pasteur having shown that in the alcoholic fermentation between 2.5 and 3% by weight of glycerol was formed of the sugar fermented. Neuberg and his co-workers in the years immediately preceding the first World War studied the mechanism of glycerol production in the alcoholic fermentation and the role played by acetaldehyde. They found that "fixing" the acetaldehyde with reagents such as sulphites, bisulphites, or compounds of the carbazide or hydrazine type resulted in a very marked increase in glycerol production. The yields of glycerol and acetaldehyde on sugar fermented in the presence of sodium sulphite were determined by Neuberg and Reinfurth (13). They found that the equation,

$$C_6H_{12}O_6 + Na_2SO_3 + H_2O = CH_3.CHO.NaHSO_3 + C_3H_8O_3 + NaHCO_3,$$

held during the fermentation and that the ratio of acetaldehyde to glycerol formed was constant at 1: 1.98 by weight. From this equation it follows that 180 gm. of sugar and 70 gm. of sodium sulphite should yield 92 gm. of glycerol (51% yield). Such yields, however, could not be attained since part of the sugar followed the normal ethanol fermentation, and the yeast could not tolerate the high sulphite concentrations necessary to give high yields of glycerol. Neuberg and Reinfurth found that even when sodium sulphite was added at the rate of 150 gm. per 100 gm. of sugar the yield of glycerol was only 36.9%. In the commercial field the sulphite process was patented by Connstein and Ludecke (2). Duchenne (3) has described commercial fermentations in which sugar-beet molasses was fermented by yeast in the presence of a mixed slurry of calcium sulphite and calcium bisulphite, giving yields of 15.3% glycerol on the initial sugar.

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Another means of increasing the production of glycerol in the yeast fermentation was by adding alkalies such as sodium carbonate, magnesium hydroxide, or alkaline phosphates. This method, (using sodium carbonate) was first patented by Eoff in 1918 (4). In his process sodium carbonate was added to the fermenting mash in a definite schedule and a specially "trained" or acclimatized strain of yeast was used. Yields of glycerol ranged from 20 to 25% on the sugar consumed.

In this fermentation it has been known for a long time that high sugar concentration favored glycerol production. Eoff, Linden, and Beyer (5) showed that 17.5 to 20% was optimum. Under these conditions they obtained yields of up to 25% on the sugar used. Similar results were found by Neish and Blackwood (11). Using a 22-23% dextrose medium with precision pH control (no sulphites) they got yields of up to 29%. These workers also found that in a pH-controlled 5% glucose medium fermented under anaerobic conditions the ratio of glycerol to ethanol by weight varied from 0.067 at pH 4 to 0.512 at pH 7.4.

No references have been found to attempts to carry out this fermentation on sulphite waste liquor, which is a medium low in sugar. Lees (8) using an enzyme-converted starchy material (5% sugar) in the presence of 4% of either magnesium or sodium sulphites got yields of 20% glycerol in three days. It was felt, therefore, that the low sugar content of the sulphite waste liquor would not be too great a disadvantage in an attempt to produce useful quantities of glycerol.

## Materials and Methods

In most runs a commercial yeast (Lallemand's) was used. Some work was done using strains of yeast from the Culture Collection of this Division; these were maintained on molasses agar slopes under mineral oil. Attempts to acclimatize one strain of yeast to the medium were unsuccessful.

Two samples of sulphite waste liquor were used, hereafter referred to as Liquor "A" and "B". Liquor "A" contained about 2.5% copper-reducing substances and 9.65% solids, and Liquor "B" had about 4.28% reducing substances and 14.4% solids. These samples were boiled for 15 min. to pasteurize them. (This treatment removed most of the free sulphur dioxide, which was of the order of 0.05%). When the samples were cool, the pH was set at 6.2 with lime and the liquor was allowed to stand for 30 min. It was then decanted from excess lime, nutrient salt added, the pH readjusted (if necessary), and the medium (without sterilization) dispensed in 150 ml. aliquots in sterile 500 ml. Erlenmeyer flasks. Gross contamination was avoided during handling and a heavy inoculum was used in every experiment. When commercial yeasts were used the inocula were made by shaking 5 gm. of yeast in 100 ml. of sterile water. For the other yeasts 5 to 10 ml. of a 24 hr. culture grown on a 3% dextrose–malt-combings medium was added to each fermentation flask. Most fermentations were done in still-culture and the temperature of incubation was 33.5-34°C.

The only salt necessary for the fermentation was 0.1% by weight of dibasic ammonium phosphate. Increasing the nitrogen or the phosphate content of the medium did not give increased yields of glycerol or higher consumption of sugar. As binding agents commercial calcium sulphite, and the mixed calcium sulphite: bisulphite slurry recommended by Duchenne (3) were tried. The latter is very acidic and since it is added as a slurry it dilutes the already low sugar content of the sulphite waste liquor. Sodium sulphite was also tried but its great solubility is a disadvantage in sulphite waste medium, which is already high in salts. Magnesium sulphite was chosen since it is rather alkaline in reaction and is soluble only to the extent of 1.25% in cold water. It was usually added to the medium two or three hours after inoculation, as recommended by Neuberg (12), and the pH readjusted to 6.1 with acetic acid.

Carbohydrates in the sulphite waste liquors were determined colorimetrically by the Sumner method (6) after clearing with zinc sulphate and sodium hydroxide. This method gave reliable results when compared with the method of Somogyi and Shaffer, as modified by Underkofler *et al.* (15). Glycerol was determined by the method of Neish and Lambert (7) using chromotropic acid and periodic acid oxidation after partition chromatography on a Celite column (10). With sulphite waste liquor the chromatographic method was particularly useful since it gave a means of separating the glycerol from compounds in the medium which reacted with chromotropic acid. Ethanol was determined by the Conway microdiffusion method (16). In both the glycerol and the ethanol determination, a blank, prepared from the treated sample of sulphite waste liquor with the appropriate amount of inoculum, was used. In the determination of ethanol no account was taken of any acetaldehyde that might have been freed from its bisulphite binding during the analysis.

## Results

### *Low Sugar Molasses Medium with Added Sulphite*

Sugar-beet molasses was used to determine the yields of glycerol that could be expected from a low-sugar medium, free from the inhibitory substances of sulphite waste liquor. A commercial yeast was used. Results are shown in Table I. Added magnesium sulphite slowed the fermentation very markedly, as demonstrated by sugar consumption. With 3% magnesium sulphite, maximum glycerol yield was reached in 41 hr. With 4, 5, and 6% it was not reached until 65 hr. The yields of glycerol based on the sugar consumed were quite high. Ethanol production dropped sharply in the presence of magnesium sulphite. Table I shows that with the exception of the control, the ratios of glycerol to ethanol were all of the order of 1: 1. This high ratio was probably due to the low sugar concentration, since Duchenne (3), using molasses media with 14% sugar, got ratios of 0.25.

### *Liquor "A" with Added Sulphite*

Similar experiments were made on Liquor "A". Table II sets out the results of one such experiment. As with the low-sugar molasses medium, added sul-

TABLE I

GLYCEROL AND ETHANOL PRODUCTION AND SUGAR CONSUMPTION BY COMMERCIAL YEAST GROWN ON A 5% SUGAR-BEET MOLASSES MEDIUM WITH VARYING AMOUNTS OF MAGNESIUM SULPHITE

(Yields expressed as gm. per 100 ml. of medium. Initial sugar = 2.34%)

| Time | 17 Hr. | | | | 41 Hr. | | | | 65 Hr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $MgSO_3$, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % |
| Control | 0.08 | 0.77 | 0.0 | 3.25 | – | – | – | – | – | – | – | – |
| 1 | 0.11 | 0.11 | 1.64 | 15.65 | 0.30 | 0.65 | Trace | 12.65* | – | – | – | – |
| 2 | 0.14 | 0.13 | 1.63 | 19.4 | 0.35 | 0.58 | Trace | 14.96* | 0.36 | 0.54 | Not determined | 15.34* |
| 3 | 0.17 | 0.14 | 1.45 | 18.6 | 0.38 | 0.50 | 0.07 | 17.00 | 0.36 | 0.43 | " | 15.34* |
| 4 | 0.14 | 0.13 | 1.56 | 17.8 | 0.35 | 0.39 | 0.40 | 17.34 | 0.43 | 0.36 | 0.13 | 19.5 |
| 5 | 0.14 | 0.11 | 1.58 | 18.6 | 0.29 | 0.36 | 0.65 | 16.77 | 0.44 | 0.39 | 0.10 | 19.42 |
| 6 | 0.12 | 0.07 | 1.62 | 16.8 | 0.30 | 0.35 | 0.74 | 18.44 | 0.43 | 0.41 | 0.13 | 19.28 |

* *Calculated on the assumption that all the sugar was used.*

TABLE II

GLYCEROL AND ETHANOL PRODUCTION, AND SUGAR CONSUMPTION BY YEAST GROWN ON SULPHITE WASTE LIQUOR "A" IN THE PRESENCE OF DIFFERENT AMOUNTS OF MAGNESIUM SULPHITE

(Yields expressed as gm. per 100 ml. of medium. Initial sugar = 2.48%)

| Time | 19 Hr. | | | | 43 Hr. | | | | 67 Hr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $MgSO_3$, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % |
| Control | 0.03 | 0.43 | 1.26 | 2.78 | 0.04 | 0.39 | 1.19 | 2.79 | – | – | – | – |
| 1 | 0.09 | 0.32 | 1.28 | 7.58 | 0.08 | 0.33 | 1.22 | 6.35 | 0.03 | 0.32 | 1.16 | 2.0 |
| 2 | 0.13 | 0.27 | 1.31 | 10.77 | 0.12 | 0.27 | 1.23 | 9.92 | 0.12 | 0.27 | 1.15 | 9.02 |
| 3 | 0.13 | 0.19 | 1.57 | 13.84 | 0.14 | 0.25 | 1.38 | 12.91 | 0.17 | 0.25 | 1.19 | 12.9 |
| 4 | (0.10) | 0.12 | 1.73 | 13.50 | 0.13 | 0.18 | 1.40 | 12.13 | 0.16 | 0.18 | 1.32 | 13.36 |
| 5 | (0.09) | 0.10 | 1.82 | 13.50 | 0.10 | 0.13 | 1.45 | 10.3 | 0.15 | 0.14 | 1.44 | 14.8 |
| 6 | 0.08 | 0.12 | 1.75 | 13.42 | 0.13 | 0.13 | 1.45 | 12.3 | 0.16 | 0.17 | 1.35 | 14.37 |

phite caused a marked falling off in ethanol production, although the utilization of sugars was not slowed as much at the lower concentrations of sulphite. The yields of glycerol based on the sugar used were not as good as those obtained with molasses. There was also more variation in the glycerol: ethanol ratio when sulphite waste liquor was used. Moreover, the sulphur compounds normally present in waste liquor as sulphonic acids had no beneficial effect on the production of glycerol, as shown by the control flasks. These produced only 2.78% glycerol, which is the amount usually formed in the ethanol fermentation by yeast.

Similar experiments with shaken flasks gave results very similar to those shown in Table II, but the fermentation was completed about 12 hr. sooner than in those conducted in still-culture.

The effect of using concentrated Liquor "A" was also determined. The liquor was concentrated to half volume in an all-glass evaporator of the type described by Bartholomew (1), giving a medium with 4.89% of copper-reducing substances. The yeast grew quite strongly in this medium, even in the presence of different amounts of magnesium sulphite. Table III brings out very clearly the effects of the added sulphite on the yeast. With increased amounts of sulphite there was a marked falling off in ethanol production, with an increase, although not to the same extent, in glycerol production. In all the flasks the yields of glycerol were low and the highest sugar consumption was only 45% of the total carbohydrate. The low glycerol yields and sugar consumption were probably due to the higher concentration of inhibitory substances and salts in this medium than in the normal strength liquor. This table also shows up an effect that has often been noticed in the course of the work: with the addition of small amounts of sulphite (about 1%), sugar consumption was more rapid than in the controls. It is important to note from this table, too, that yeast will grow strongly on concentrated sulphite waste liquor to give good yields of ethanol.

*Liquor "A" with Added Molasses*

The sugar content of Liquor "A" was doubled by the addition of sugar-beet molasses, with the results shown in Table IV. Comparison of this table with Table I shows that the inhibitory effects of the added sulphite and of the sulphite waste liquor seem to be cumulative. The yields of glycerol on sugar used were only one-third to one-half of those on a molasses medium. In the presence of higher concentrations of magnesium sulphite (2.66 and 4%) there was a marked slowing in the rate of sugar consumption, although, as in the previous experiments, the addition of 1.33% sulphite to the medium stimulated sugar consumption. It appears that the addition of molasses to the medium is definitely disadvantageous, in contrast with the effects of added molasses on the 2, 3-butanediol fermentation of sulphite waste liquor (9).

*Liquor "B"*

This sample of sulphite waste liquor was from a mill manufacturing pulp mainly for a viscose plant and was considerably higher in carbohydrate than

TABLE III

GLYCEROL AND ETHANOL PRODUCTION, AND SUGAR CONSUMPTION BY YEAST IN THE PRESENCE OF DIFFERENT AMOUNTS OF MAGNESIUM SULPHITE IN LIQUOR "A" CONCENTRATED TO HALF VOLUME

(Yields expressed as gm. per 100 ml. of medium. Initial sugar = 4.89%)

| Time | 20 Hr. | | | | 44 Hr. | | | | 68 Hr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $MgSO_3$, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % |
| Control | 0.04 | 0.50 | 3.57 | 3 | 0.08 | 0.71 | 2.98 | 4.2 | 0.07 | 0.68 | – | – |
| 1.33 | 0.10 | 0.56 | 3.13 | 5.69 | 0.12 | 0.69 | 2.67 | 5.41 | 0.12 | 0.77 | – | – |
| 2.66 | 0.10 | 0.36 | 3.43 | 6.85 | 0.16 | 0.47 | 3.17 | 9.3 | 0.22 | 0.58 | 3.08 | 12.15 |
| 4 | 0.11 | 0.26 | 3.81 | 10.20 | 0.14 | 0.30 | 3.54 | 12.67 | 0.21 | 0.36 | 3.51 | 15.2 |

TABLE IV

GLYCEROL AND ETHANOL PRODUCTION, AND SUGAR CONSUMPTION BY YEAST IN THE PRESENCE OF DIFFERENT AMOUNTS OF MAGNESIUM SULPHITE IN LIQUOR "A" MEDIUM WITH 5% BY WEIGHT ADDED SUGAR-BEET MOLASSES

(Yields expressed as gm. per 100 ml. of medium. Initial sugar = 5.49%)

| Time | 20 Hr. | | | | 43 Hr. | | | | 67 Hr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $MgSO_3$, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % |
| Control | 0.06 | 0.59 | 3.78 | 3.5 | 0.09 | 1.28 | 1.95 | 2.54 | 0.09 | 1.53 | 1.22 | 2.1 |
| 1.33 | 0.13 | 0.72 | 3.28 | 5.88 | 0.22 | 1.21 | 1.60 | 5.65 | 0.22 | 1.50 | 1.11 | 5.02 |
| 2.66 | 0.10 | 0.31 | 4.02 | 6.8 | 0.25 | 0.75 | 2.71 | 9.00 | 0.25 | 1.14 | 2.03 | 7.22 |
| 4 | 0.07 | 0.18 | 4.45 | 6.73 | 0.17 | 0.31 | 3.80 | 10.00 | 0.23 | 0.54 | 3.29 | 10.47 |

TABLE V

GLYCEROL AND ETHANOL PRODUCTION, AND SUGAR CONSUMPTION ON LIQUOR "B" IN THE PRESENCE OF DIFFERENT AMOUNTS OF MAGNESIUM SULPHITE

(Yields expressed as gm. per 100 ml. of medium. Initial sugar = 4.56%)

| Time | 21 Hr. | | | | 45 Hr. | | | | 69 Hr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $MgSO_3$, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % | Glycerol, % | Ethanol, % | Residual sugar, % | Yield glycerol on sugar used, % |
| Control | 0.06 | 0.72 | 2.46 | 2.86 | 0.11 | 0.89 | 2.00 | 4.29 | 0.08 | 0.95 | 1.85 | 2.95 |
| 1 | 0.13 | 0.74 | 1.92 | 5.07 | 0.19 | 0.76 | 1.80 | 6.88 | 0.15 | 0.86 | (1.93) | – |
| 2 | 0.18 | 0.57 | 2.20 | 7.63 | 0.32 | 0.66 | 1.91 | 12.08 | 0.32 | 0.77 | 1.74 | 11.34 |
| 3 | 0.08 | 0.13 | 3.35 | 6.61 | 0.31 | 0.47 | 2.40 | 14.35 | 0.30 | 0.66 | 2.00 | 11.72 |
| 4 | 0.16 | 0.30 | 2.90 | 9.64 | 0.36 | 0.54 | 2.03 | 14.23 | 0.35 | 0.64 | 1.74 | 12.44 |
| 5 | 0.15 | 0.26 | 3.15 | 10.71 | 0.37 | 0.45 | 2.39 | 17.05 | 0.34 | 0.56 | 2.00 | 13.28 |
| 6 | 0.10 | 0.17 | 3.32 | 8.06 | 0.25 | 0.34 | 2.66 | 13.16 | 0.36 | 0.58 | 1.90 | 14.28 |

Liquor "A". Table V shows that reasonable yields of glycerol were obtained with 2, 3, 4, and 5% added magnesium sulphite in 45 hr. Beyond this time, however, glycerol production stopped, except for the flasks with 6% sulphite, and further sugar used went into the production of ethanol.

## Discussion

This work has shown that while it is possible to ferment samples of sulphite waste liquor with yeast in the presence of binding agents the yields of glycerol are low. However, even in the presence of large amounts of binding agent, a great deal of the sugar fermented goes to ethanol. The addition of sulphites slows up the fermentation very markedly. A 5% sugar-beet molasses medium was completely fermented in 17 hr., while the same medium with 6% added magnesium sulphite was not completely fermented in 65 hr. (Table I). In the samples of sulphite waste liquor used the amount of sugar fermented, even in the controls, has been relatively low, rarely going above 50%. These considerations, and also the difficulty of recovering such small quantities of glycerol from a high-solids material like sulphite waste liquor, indicate that the glycerol fermentation on this medium was of very doubtful value.

The method, however, might be more suitably applied to other waste materials such as citrus-waste press juice (14) in which the ratio of sugar to nonsugar solids is more favorable (6% sugar, 4% nonsugar solids).

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# THE ABRASION RESISTANCE OF SULPHURIC ACID ANODIC FILMS ON ALUMINIUM AND ITS ALLOYS[1]

By R. C. Spooner


## Abstract

The standard American Society for Testing Materials abrasive blast technique, was employed to determine the abrasion value of anodic coatings produced on aluminium alloys by anodizing in sulphuric acid solution and water sealing. The effect on the abrasion value of five process variables, anodizing time, sealing time, air aging, current density, and electrolyte temperature was determined. Increased film thickness produced by lengthened anodizing time, rising current density, or lowered electrolyte temperature augmented the abrasion value. Increasing periods of water sealing or air aging of unsealed coatings lowered the abrasion values. Increased current density increased the abrasion coefficient.

Only slight differences were found in the abrasion value of anodic films on 99.99%, 99.76%, 2S and 3S aluminium alloys. A slight increase was determined with 50S while with 24S considerable decrease was observed.


## Introduction

The abrasion resistance of an aluminium surface can be increased greatly by suitable anodic treatment to produce a layer of aluminium oxide much thicker than the normal surface oxide film. This increased resistance to abrasion is of great value in many applications where rubbing and frictional contacts must be withstood.

Schuh and Kern (10) employed an abrasion by impingement technique to measure the abrasion resistance of organic protective coatings. This work was followed by Edwards (5) and Arlt (2) who modified the technique and applied it to anodic films. The latter's work formed the basis for the standard A.S.T.M. (1) and British Standard (3) abrasive blast techniques.

Two major effects were shown by Arlt (2), (1) the steady increase in abrasion resistance with rising film thickness produced by anodizing for longer times or at higher current densities, and (2) the sharp decrease caused by sealing the film in water or a sodium dichromate solution.

Recently, Kronsbein (6) has shown that the abrasion value of anodic film on alloys 2S-0 and 52S-0 decreases with rising electrolyte temperature and rises with increasing current density. No details were given of the abrasive blast conditions used or the specific results obtained.

Mauksch and Budiloff (9) have described another technique in which the anodic coating is moved to and fro under a hard metal pointer until the coating is penetrated. Taylor (12) has summarized results thus obtained on films anodized for the most part in oxalic acid. The abrasion resistance increased

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with film thickness. The presence of appreciable amounts of copper, zinc, or silicon in the alloy causes lower abrasion resistance. Magnesium does not adversely affect the abrasion characteristics.

A further technique is the use of the Taber Abraser (11) which provides for a sliding and rotating contact between two abrasive wheels and a test specimen which rotates on a horizontal plane under the wheels. This procedure is slow and tedious when applied to anodic coatings because of their high abrasion resistance.

An abrasive blast technique was employed to confirm the results of Arlt and Kronsbein on the influence of three anodizing variables, anodizing time, current density, and electrolyte temperature on the abrasion resistance of sulphuric acid anodic films. Two other variables, sealing time and the influence of air aging of unsealed films were also included. In addition, the abrasion resistance of coatings on six common aluminium alloys was measured.

## Experimental Procedures

(1). *Materials Used*

(*a*). *Metal*

The chemical analyses for the alloys used are shown in Table I.

Alumilite sheet (99.7% aluminium clad on 3S) was used for all tests except where other alloys are specifically indicated. This material is widely used in Canada because of its superior anodizing quality.

The test panels were generally of 6 in. × 9 in. × 0.064 in. dimensions but in two series an additional set of 3 in. × 5 in. × 0.064 in. panels was also employed. The 50S extrusions were approximately 20 in. × $2\frac{1}{2}$ in. × 0.125 in.

(*b*). *Abrasive*

In compliance with A.S.T.M. procedure, silicon carbide abrasive (Canadian Carborundum Co., Niagara Falls, grit No. 180 GG) was screened to obtain the fraction passing 170 mesh and retained on the 200 mesh Tyler standard screen. A Ro-Tap electrically driven mechanical shaker was employed for one hour followed by hand shaking the material retained on the 200 mesh screen for five minutes.

(2). *Panel Preparation*

A 1 in. strip around each panel immediately adjacent to the top edge, was "stopped off" by application of Scotch Plastic Electroplating Tape (Minnesota Mining and Manufacturing Co., St. Paul, Minn., No. 470). The tape was perforated at a point on each of the two side edges to allow direct contact between the clamp on the anodizing rack and the bare metal.

The cleaning treatment included immersion for five minutes in a cleaning solution of the following composition at 65°C.:

| | |
|---|---|
| Sodium carbonate | 18 gm. per liter |
| Trisodium phosphate | 18 gm. per liter |
| Santomerse No. 1 | 1 gm. per liter |

This was followed by etching in sodium hydroxide solution (10%) at 65°C. for 30 sec. and a 15 sec. dip in cold 50% nitric acid.

Panels were anodized individually in a 15% by weight sulphuric acid solution* at 21°C. and, except where otherwise indicated, at 15 amp. per sq. ft. current density with a moderate degree of air agitation. The panels were immersed in the electrolyte only up to the lower edge of the insulating tape so that the clamp was out of the solution.

After anodizing the films were sealed by immersion of the panel in boiling water (pH 5.9 ± 0.2). The treatment time varied but usually equalled the anodizing time.

An adequate cold water rinse was provided after each of the individual treatments outlined above. Deionized water (less than 12 p.p.m. dissolved materials) was employed throughout the work.

With the large 6 in. × 9 in. panels the top inch of unanodized metal was removed. The 6 in. × 8 in. panel thus formed was sheared to make four 3 in. × 4 in. panels. One of the four specimens was used initially for the abrasion tests while the others were reserved for check determinations. The 3 in. × 5 in. panels were not sectioned. The long 20 in. extrusion was cut transversely into four sections, but the lower section used initially.

Series of specimens were prepared as outlined below followed by abrasion testing.

*Anodizing time:* Panels were anodized for periods of 10 to 60 min. at a current density of 16.5 amp. per sq. ft. and then water sealed for a period equal to their anodizing time.

*Sealing time:* Panels were anodized for 30 min. and duplicate (or triplicate) panels were sealed for periods varying from 0 to 60 min.

*Air aging:* Unsealed panels anodized for 30 min. were water rinsed, acetone rinsed, and air-dried for five minutes prior to abrasion testing. Tests were repeated at periods up to 30 days air aging. One panel was stored in a desiccator between abrasion tests.

*Current density:* Two series of panels were anodized for 20 min., at current densities of 12 to 24 amp. per sq. ft. The first was sealed for 20 min., and the second for 60 min

*Electrolyte temperature:* Two series of panels were anodized for 20 min. with an electrolyte temperature of 21°, 25°, and 30°C. and sealing times of 20 min. (Series A) or 60 min. (Series B).

*Alloy:* Panels of alloys listed in Table I were anodized for 20 min. followed by sealing for 20 min.

* *A semicommercial anodizing tank of 225 gal. capacity with automatic temperature regulation to ±1°C. was employed.*

TABLE I

CHEMICAL ANALYSIS OF ALLOYS USED FOR ABRASION TEST SPECIMENS

| Alloy | % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | Fe | Mg | Mn | Si | Ti | Zn | Cr | Al (by diff.) |
| Super Purity | 0.001 | 0.004 | <0.001 | <0.001 | <0.002 | <0.001 | <0.001 | <0.001 | 99.99 |
| Alumilite* | 0.005 | 0.13 | 0.001 | 0.001 | 0.09 | 0.008 | – | – | 99.76 |
| 2S–¾H | 0.02 | 0.42 | – | – | 0.29 | 0.01 | – | – | 99.26 |
| 3S–½H | 0.08 | 0.40 | – | 1.12 | 0.23 | 0.01 | – | – | 98.16 |
| 24S–T | 4.48 | 0.39 | 1.45 | 0.59 | 0.30 | 0.01 | – | – | 92.78 |
| 50S–T | 0.03 | 0.32 | 0.74 | 0.01 | 0.33 | – | – | – | 98.57 |

* *Cladding Layer Analysis.*

(3). *Abrasion Testing*

Except for the few minor variations described below, the apparatus and procedure were as listed in the A.S.T.M. procedure (1). Preliminary work showed that it was tedious and time consuming to adjust the apparatus to duplicate completely the listed conditions.* The following conditions were adopted to provide convenient and reproducible test conditions:

| | |
|---|---|
| Manometer pressure | 10 ± 0.1 cm. mercury |
| Abrasive flow rate | 59 ± 2 gm. per min. |

The rate of air flow was less important than these two conditions and was approximately 3.5 cu. ft. per min.

The A.S.T.M. specified end point was adopted, i.e. the appearance of a dark spot 2 mm. in width in the center of the wear pattern. Fig. 1 shows five typical wear spots. The central darker area is the spot whose horizontal width was measured. The spots were at least one-quarter inch and generally much farther away from the edge to avoid any possible "edge effect" in the film.

The abrasive hopper was weighed before and after each test. The difference in weight was designated as the "abrasion value" of the spot tested. The average value for five spots on one side of the specimen** was considered the "abrasion value" for the panel.

In all cases the time required to reach the wear spot end point was measured and the average rate of flow of abrasive determined. The departure of this value from the set rate of abrasive flow revealed any major irregularities in air or abrasive flow thus necessitating a further test.

* *The difficulty in completely duplicating specified conditions has been recognized in the A.S.T.M. (1) and the British Standards (3) which suggest the use of panels anodized under standard conditions for interlaboratory correlation of test conditions.*

** *In the initial work, five determinations were made both on the front and back sides. Because of the good agreement between the averaged values of the two sides, this was reduced to measurements on only one side.*

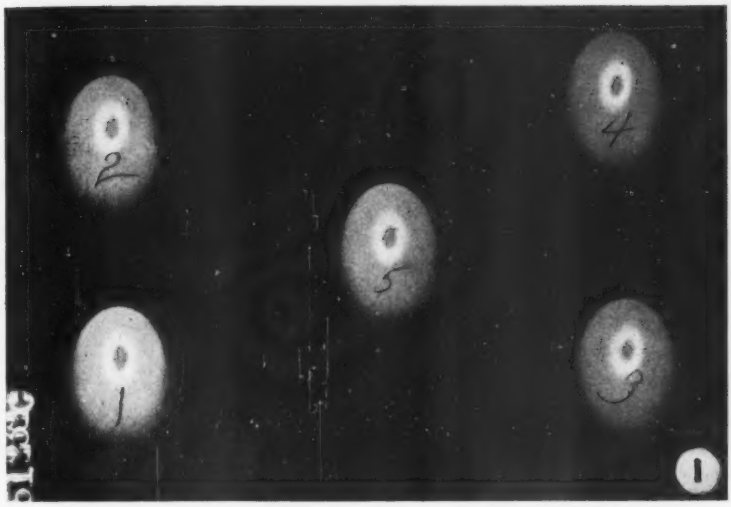

FIG. 1. *Abrasion test wear spots (approx. 1×).*

Another term, the "abrasion coefficient" was calculated as follows:

$$\text{Abrasion coefficient } (\text{gm.}/\mu) = \frac{\text{abrasion value (gm.)}}{\text{coating thickness } (\mu)}.$$

This unit served as a measure of the specific abrasion characteristics and thus permitted direct comparison of the results from films of varying film thickness.

Measurements were made under the normal laboratory conditions of temperature and humidity. Although in testing organic coatings definite values are set for these two variables, it was considered that small variations in their values during measurements would have only a minor effect on the abrasion resistance of anodic coatings, especially those which were sealed.

(4). *Film Thickness Determination*

A section of each panel, selected between the abraded spots and well away from original edges of the anodized panel, was mounted, polished, and the anodic coating thickness determined by the customary metallographic technique. Values reported were the average of 10 individual determinations, each accurate to within $\pm 0.3\mu$.

## Results

(1). *Anodizing Time*

The abrasion values rose as the film thickness increased with lengthening periods of anodizing (Table II).

TABLE II

THE EFFECT OF ANODIZING TIME ON THE ABRASION RESISTANCE

| Anodizing time (min.) | Abrasion value (gm.) | Film thickness ($\mu$) | Abrasion coefficient (gm./$\mu$) |
|---|---|---|---|
| 3 | x* | 1.5 | — |
| 10 | 78 | 6.5 | 12 |
| 20 | 178 | 11.5 | 15 |
| 30 | 300 | 18.0 | 17 |
| 60 | 563 | 39.8 | 14 |

* *Too small to be accurately determined under test conditions.*

The abrasion coefficients advanced from 12 to 17 and then declined to 14 as anodizing was prolonged to 60 min. The differences, particularly among the three thicker films, although not large, are significant.* The film thickness increased approximately linearly with anodizing time thus not indicating any change in the rate of film growth which might explain the changes in the abrasion coefficient.

The observed increase in abrasion value is in agreement with the results reported by Arlt (2) who found that with both unsealed, water sealed, and sodium dichromate solution sealed panels, the abrasion resistance increased with anodizing time. The unsealed panels had higher resistance than the dichromate films which in turn showed resistance above that of the water sealed panels. Arlt suggested that these differences "may be related to the degree of hydration of the coating" but does not discuss this effect further. A possible cause for the difference between the two types of sealing is the lower pH value of the dichromate solution (probably 4-4.5) and its effect in producing a decreased degree of water hydration. This has been discussed by Tomashov and Tyukina (13).

(2). *Sealing Time*

It is well known that water sealing is accompanied by an appreciable weight gain due to the hydration and adsorption of water by the anodic film. This process is accompanied by, and appears responsible for, the decrease in abrasion values indicated in Table III.

Water sealing even for very brief periods of one minute caused a large decrease in the abrasion coefficient. As sealing time was prolonged, the rate of decrease became much less until the sealing for longer periods caused little, if any, further change.

The averaged abrasion coefficients are plotted in Fig. 2 to illustrate the change in the abrasion characteristics produced by water sealing.

* *Confirmed by statistical evaluation.*

TABLE III
THE EFFECT OF SEALING TIME ON ABRASION RESISTANCE

| Sealing time (min.) | Abrasion value (gm.) | Film thickness (μ) | Abrasion coefficient (gm./μ) | |
|---|---|---|---|---|
| | | | Individ. | Av. |
| 0 | 413 | 14.9 | 27.7 | |
| 0 | 383 | 13.2 | 29.0 | |
| 0 | 395 | 14.1 | 28.0 | 28 |
| 1 | 310 | 15.3 | 20.2 | |
| 1 | 385 | 15.5 | 24.8 | |
| 1 | 362 | 17.2 | 21.0 | 22 |
| 5 | 304 | 15.8 | 19.2 | |
| 5 | 323 | 15.0 | 21.5 | 20 |
| 10 | 289 | 15.7 | 18.4 | |
| 10 | 320 | 15.1 | 21.2 | 20 |
| 30 | 204 | 13.6 | 15.0 | |
| 30 | 281 | 13.8 | 20.4 | |
| 30 | 251 | 15.6 | 16.1 | 17 |
| 60 | 244 | 15.0 | 16.3 | |
| 60 | 247 | 14.8 | 16.7 | 16 |

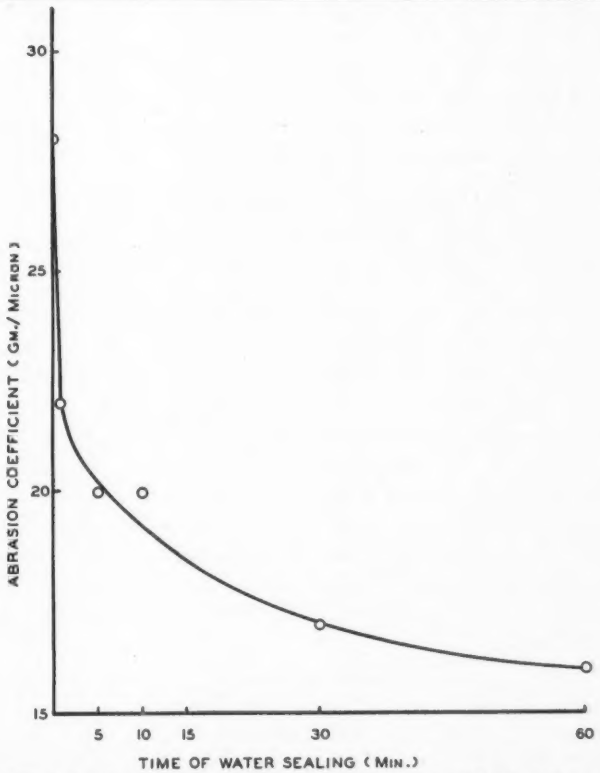


FIG. 2. *Effect of water sealing on the abrasion coefficient of sulphuric acid anodic films.*

(3). *Air Aging*

The effect of air aging in lowering the abrasion characteristics of the freshly formed unsealed anodic film* is indicated by the results summarized in Table IV.

TABLE IV

EFFECT OF AIR AGING ON ABRASION RESISTANCE OF UNSEALED ANODIC COATINGS

| Storage in: | Period of aging | Abrasion value (gm.) | Film thickness ($\mu$) | Abrasion coefficient (gm./$\mu$) |
|---|---|---|---|---|
| Air | 10 min. | 413 | | 28 |
| | 1.7 days | 365 | 14.9 | 24 |
| | 15 days | 357 | | 24 |
| | 30 days | 337 | | 23 |
| Desiccator | 10 min. | 383 | | 29 |
| | 1.7 days | 320 | 13.2 | 24 |
| | 15 days | 321 | | 24 |
| | 30 days | 325 | | 25 |

In the first example aging for a period of 30 days lowered the abrasion value about 18%, from 413 to 337 gm. The second panel was stored in a desiccator but decreased from 383 to 325 gm. (i.e. about 15%) in a similar period. The loss in abrasion value with this panel occurred only during the first 1.7 days of storage, after which the value remained essentially constant. This suggests that the initial decrease was due to a hydration and/or adsorption of the water in the pores of the film by the aluminium oxide. Once this was completed the abrasion value remained constant. With the first panel continued air exposure would allow hydration to continue at a decreased rate.

(4). *Current Density*

There is a steady increase in abrasion value as the film thickness grows with rising current density (Table V). The steady increase in the abrasion coefficient indicates that the coatings produced at higher current density have improved abrasion characteristics.

At higher current densities thicker films are formed in a given time. The rise in current density increases both the rate of anodic film growth and, to a lesser extent, the rate of chemical dissolution of the coating by the electrolyte. The increase in the latter effect is due, it is suggested, to the larger surface area provided by the thicker film and by other changes in the surface conditions during anodizing. The result is the formation of a thicker coating with different film characteristics including, probably, decreased porosity and a higher abrasion coefficient.

The lower values for the series sealed for the longer time indicates again the effect of increased sealing time in lowering the abrasion resistance.

* *Some indication was obtained that this air aging effect is present to a small degree with anodic films water sealed for periods of five minutes or less.*

TABLE V

THE EFFECT OF CURRENT DENSITY ON THE ABRASION RESISTANCE

| Current density amp./sq. ft. | Sealing time (min.) | Abrasion value (gm.) | Film thickness ($\mu$) | Abrasion coefficient (gm./$\mu$) |
|---|---|---|---|---|
| Series A | | | | |
| 12 | 20 | 115 | 8.2 | 14 |
| 15 | 20 | 184 | 11.0 | 17 |
| 18 | 20 | 225 | 14.0 | 16 |
| 24 | 20 | 332 | 16.4 | 20 |
| Series B | | | | |
| 12 | 60 | 88 | 8.0 | 11 |
| 18 | 60 | 206 | 14.0 | 15 |
| 24 | 60 | 296 | 18.5 | 16 |

These trends differ in some respects from the results reported by Arlt (2) who measured abrasion resistance of films produced at current densities from 5 to 35 amp. per sq. ft. Although the abrasion value advanced steadily with rising film thickness, the abrasion coefficient varied considerably and no definite trend was apparent.

(5). *Electrolyte Temperature*

With rising electrolyte temperatures thinner films are produced in a given time and this is accompanied by a fall in the abrasion value (Table VI).

TABLE VI

THE EFFECT OF ELECTROLYTE TEMPERATURE ON THE ABRASION RESISTANCE

| Electrolyte temperature (°C.) | Sealing time (min.) | Abrasion value (gm.) | Film thickness ($\mu$) | Abrasion coefficient (gm./$\mu$) |
|---|---|---|---|---|
| Series A | | | | |
| 21 | 20 | 184 | 11.0 | 17 |
| 25 | 20 | 163 | 10.0 | 16 |
| 30 | 20 | 148 | 9.2 | 16 |
| Series B | | | | |
| 21 | 60 | 182 | 11.2 | 16 |
| 25 | 60 | 142 | 10.0 | 14 |
| 30 | 60 | 121 | 9.0 | 13 |

In Series A the abrasion coefficient remains approximately constant, thus suggesting little, if any, change in the abrasion characteristics of the coating apart from the effect due to decreased film thickness. However, in Series B there is a small decrease in the abrasion coefficient as the temperature is increased. The values of Series B panels are slightly, but consistently, lower than those for the Series A panels anodized at the same electrolyte temperature. This trend is in accord with the results reported above on the effect of water sealing time in lowering the abrasion coefficient.

In commercial anodizing practice, higher electrolyte temperatures are frequently employed to produce a more "porous" coating, resulting in a deeper dyed color. This increased porosity would be expected to decrease the abrasion coefficient of the coating. Only the Series B results support this expectation.

(6). *Abrasion Values of Anodic Films on Various Alloys*

The values obtained for six aluminium alloys are listed in Table VII. The abrasion coefficients indicate clearly the marked inferiority of the anodic coating on 24S. The other five alloys show only a slight spread of values with 50S possessing slightly superior abrasion characteristics.

TABLE VII

THE ABRASION RESISTANCE OF ANODIC FILMS ON VARIOUS ALUMINIUM ALLOYS

| Alloy | Anodizing time (min.) | Abrasion value (gm.) | Film thickness ($\mu$) | Abrasion coefficient (gm./$\mu$) |
|---|---|---|---|---|
| Alumilite | 20 | 179 | 10.5 | 17 |
| Super Purity | 20 | 188 | 11.1 | 17 |
| 2S | 20 | 163 | 10.1 | 16 |
| 3S | 20 | 159 | 9.5 | 17 |
| 24S | 20 | 68 | 7.2 | 9 |
| 50S | 20 | 190 | 9.9 | 19 |

The low abrasion resistance of the anodic film on 24S is in agreement with the fact that such coatings differ in many properties from the coatings on other alloys. The deeper color produced on dyeing is one example of this difference.

## Discussion

(1). *The Abrasive Blast Method*

The reproducibility of the abrasive blast test results is affected by the following factors: 1. Variations in local abrasion values over the panel surface; 2. Variations in the test conditions.

The abrasion value depends upon both the thickness and the abrasion coefficient of the coating. With normal conditions, the film thickness varies only slightly from point to point owing to the excellent throwing power found in anodizing. For instance, with one typical panel, a metallographic examination of the film thickness at numerous points showed all values within the range of $16 \pm 1\mu$. Under normal conditions, the abrasion coefficient would be expected to vary only to a very small degree, particularly with high purity metal of fine and uniform grain size, as was the case with the Alumilite sheet employed in the bulk of the experimental work. Thus, it would appear that the reproducibility of the results is influenced only slightly, if at all, by variations in local abrasion values. This leaves the second factor, variations in test conditions, for consideration.

The maximum deviation from the mean value of the results (usually five) on a panel was generally less than 10%. In much of the work this was reduced to 2-5%. In a few isolated cases, all with one operator, the scatter was somewhat greater. However, the averaged values for these panels were in excellent agreement with duplicate panels with the normal degree of scatter. Apart from this, no "operator effect" was noted.

Some of the factors contributing to these deviations are:

(*a*). *Air pressure:* Tests confirmed, as expected, the findings of Schuh and Kern (10) that the abrasion value decreases as the air pressure is increased. As high pressures are approached there is a smaller decrease in the rate of change of the abrasion value. However, it was estimated that variations of 0.1 cm. in the assigned pressure of 10 cm. would change the abrasion value by only 1%.

(*b*). *Rate of abrasive flow:* Test results indicated that variations within the set limits (59 ± 2 gm. per min.) had relatively little effect on the abrasion values.

(*c*). *Variation in the wear spot end point:* The visual determination of the end point* was undoubtedly a major cause in the variation of results among the several determinations on individual panels. However, approximately 60-75% of the total abrasive required flows prior to the appearance of the beginnings of a wear spot,** then this widens rapidly. Any error due to end point determination affects only the latter part of the procedure. An occasional preventive measure was the careful measurement, under low power magnification, of wear spot diameters.

(2). *Relationship of Abrasion Coefficient to Anodizing Variables*

The abrasion value of anodic coatings depends upon the film thickness and the abrasion coefficient. The film thickness requires no comment. It is dependent upon anodizing conditions and may vary widely at choice. The effect of various anodizing variables on the abrasion coefficient is, however, less certain. The results presented above, series by series, each illustrate the effect of essentially only one variable. In all cases it is the trend rather than the individual values that should be emphasized. These results indicate that the abrasion coefficient is affected to a major extent by water sealing, and to a smaller degree by air aging (of unsealed films), alloy (in some cases), current density, and anodizing time. The effect of electrolyte temperature, although not listed above, must also be considered.

The effect of water sealing in rapidly decreasing the abrasion coefficient is most striking. As is well known, the unsealed coating produced by anodizing in sulphuric acid solutions is a layer of amorphous aluminium oxide with a

* *Microscopic examination of a cross section through a typical 2 mm. wear spot showed a complete loss of anodic film for 1.4 mm. distance. There was an additional section on either side with a very thin residual anodic coating of visual appearance similar to that of the exposed metal.*

** *Initial penetration of the coating as indicated by the formation of a black spot is the end point specified by BIS 1615 (3).*

small water and sulphate content, which has the high degree of hardness and abrasion resistance typical of this oxide. Water sealing is accompanied by a small weight gain due to the formation of alumina alpha-monohydrate and probably to some water adsorption. This change produces a "swelling" effect due to the volume increase, which decreases the diameter of the myriad number of very fine pores* present. The sealing process contributes greatly increased corrosion resistance.

The fact that the abrasion coefficient is so greatly lowered by water sealing indicates that sealing does not produce just a thin hydrated layer or "skin" on the surface of the pores for this would have but a slight effect on the abrasion coefficient, but rather that hydration proceeds to a considerable extent in the coating itself. The decrease in the abrasion coefficient is more rapid at the start and eventually slows to a very small rate. This is in agreement with the results of unreported work in this laboratory on the weight gain in water sealing.

In commercial anodizing practice it is recognized that thicker anodic coatings require longer sealing periods to secure an equivalent degree of sealing. It follows that in the various series described above with a fixed sealing period the degree of sealing produced was not constant but fluctuated with changes in the film thickness. It has been shown also that the time or degree of sealing directly affects the abrasion coefficient. Thus in some series variations in abrasion coefficient are due to more than the one variable previously emphasized. For instance, Table V, Series A, lists coatings produced by current densities of from 12 to 24 amp. per sq. ft. and varying in film thickness from 8.2 to 16.4 $\mu$, but all sealed for 20 min. The time of sealing per unit thickness decreased from about 2.4 to 1.2 min. per $\mu$. It is suggested, for example, that this effect has been in part responsible for the increase in abrasion coefficient with rising current density as the film thickness increased with a consequent reduced degree of sealing. In the series on the effect of anodizing time, electrolyte temperature and alloy, the variations in the time of sealing per unit thickness are smaller. In addition, the period of water sealing employed (equal or greater than the anodizing time) was long enough to seal the film to an extent that, as indicated in Fig. 2, small variations in the degree of sealing would have only a minor effect on the abrasion resistance. Thus in these series this effect would not alter the trends already noted.

Arlt (2) also has mentioned this additional variable. He found that 10 and 20 min. coatings had higher abrasion coefficients than the 30 min. coatings.** These had all been water sealed for periods equal to their respective anodizing times. Arlt suggested that this variation "may be due to the shorter sealing time employed for the thinner coatings and may indicate incompleteness of seal of these inner coatings." However, this effect was not shown by another

** One estimate based upon gas adsorption measurements (4) with sulphuric acid anodic films is that there are 1.55 × $10^{11}$ pores/cm.$^2$ with an average pore diameter of about 110 A°. Sealing in the case of chromic acid films decreased the real surface area by up to 90%.*

*** 129, 111, and 95 gm. per 0.001 in. respectively. This is equivalent to 5.1, 4.4, and 3.7 gm. per $\mu$. Arlt's values are all considerably lower than those reported above owing to higher electrolyte temperature (35°C.), different alloy, and higher abrasive blast pressure (12 cm. mercury).*

group of his panels treated in similar fashion except for the substitution of sodium dichromate solution for water sealing.

Lewis (7) has referred to the capacity of chromic acid anodic films (probably sealed only by a brief warm water rinse), to "age-harden becoming very hard after a time." She has suggested (8), (1) that possibly this property is the reason for the stipulation in British Standard, 1615.1949, (3) that the standard chromic acid anodized specimens for abrasion testing be used within 24 hr. of their preparation, and (2) that the sealing agent may play a part in the hardening. This "age-hardening" and its probable effect in increasing the abrasion coefficient of chromic acid films is in contrast to the effect of "air aging" in lowering the abrasion coefficient of unsealed sulphuric acid anodic films discussed above (Table IV).

## Acknowledgment

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# REDUCTION OF THE VANADIUM CONTENT OF RESIDUAL PETROLEUM FUELS BY SOLVENT PRECIPITATION[1]

By W. Sacks[2]

## Abstract

The removal of vanadium compounds from residual petroleum fuels of various crudes by asphaltene precipitation has been studied. Vanadium is precipitated with the *n*-pentane asphaltenes (83-95% with 6:1 ratio of solvent to fuel) together with the major portion of iron and nickel compounds. Comparative precipitations on a Venezuelan fuel with petroleum ether (b.p. 30-60°C.), naphtha (b.p. 75-120°C.), acetone, diethyl ether, *n*-pentane, and ethyl acetate showed that the amount of vanadium removed is approximately proportional to the asphaltene yield but the naphtha fraction did not remove any appreciable amount of vanadium.

## Introduction

The use of residual petroleum fuels in gas turbine engines has increased interest in the inorganic constituents of these fuels which lead to ash deposition and corrosion of alloy steels at high temperatures (4). These effects have been associated most frequently with vanadium, a common constituent of petroleum ash and very often present in large amounts. In the combustion process the vanadium compounds may be converted to low-melting vanadium pentoxide or vanadates which deposit readily and attack the protective oxide film of alloys.

Residual fuels are generally regarded as colloidal dispersions of high molecular weight substances called asphaltenes in an oil medium (7). Their properties depend both on the crude oil and on the refinery processes which yield the residues from which they are produced. The work of Treibs (11, 12) showed that vanadium occurs as a porphyrin complex in many crude oils. Iron porphyrins were also identified. These substances were found to be only slightly soluble in common solvents. The complexes exhibited considerable stability to heat and did not react readily. Table I shows the vanadium contents of some typical No. 6 residual fuels (the heaviest grade normally utilized) from Canadian refineries.

The addition of certain solvents to these dispersions precipitates asphaltenes, the quantity and nature of which vary with the solvent and the conditions of precipitation (principally temperature, ratio of solvent to fuel). This behavior follows a "surface tension rule" (6). Solvents with a surface tension below about 24 dynes cm.$^{-1}$ (25°C.) act as precipitants; those above dissolve the dispersions without precipitation. In a series of hydrocarbon solvents the yield of asphaltenes is larger the lower the surface tension. Precipitants of high sur-

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TABLE I

VANADIUM CONTENTS OF SOME CANADIAN NO. 6 RESIDUAL FUELS

| Crude | Fuel composition | Vanadium, p.p.m. wt. |
|---|---|---|
| Venezuela | 100% thermally cracked residuum | 146 |
| Arabian | 60% residuum + cycle oils | 143 |
| California | 100% thermally cracked residuum | 25 |
| Redwater | 100% thermally cracked residuum | 12 |
| Leduc | 100% thermally cracked residuum | 2.5 |

face tension separate only high molecular weight asphaltenes while those of lower surface tension separate, in addition, asphaltenes of smaller molecular size. Polar solvents such as acetone are not selective to asphaltenes and the precipitates contain oil and wax fractions (5) but ethyl acetate apparently does not precipitate oil or wax fractions (2).

Since the porphyrin complexes are of relatively high molecular weight it would be expected that precipitation would occur with the asphaltenes. Recent data by Howes (3) on several Middle East residues of high vanadium content show this to be true. Propane (used for deasphalting residues for catalytic cracking) was found to yield an oil containing no appreciable amount of vanadium. Paraffin hydrocarbon solvents containing 4-7 carbon atoms (low surface tension) were also studied and were found to precipitate vanadium with the asphaltenes, the concentration of vanadium in the deasphalted oil varying with the yield of precipitate.

In the present work the removal of vanadium from residual fuels of various crudes and vanadium contents was studied, using both hydrocarbon and polar solvents. Since the corrosive nature of vanadium ashes will probably depend on the presence of other substances which act as diluents, the removal of iron and nickel compounds commonly present with vanadium has also been examined.

## Experimental

*Precipitation of Vanadium, Iron, and Nickel with Pentane Asphaltenes*

A series of No. 6 residual fuels from different crudes was treated with six volumes of *n*-pentane per volume of fuel, refluxed for one hour on a steam bath, and allowed to stand overnight. The solutions were decanted through a Buchner filter and any remaining tarry matter treated with fresh solvent until only dark solids remained. The asphaltene solids were collected on the filter, washed with solvent until the washings were only faintly colored, and the combined filtrate and washings evaporated on a steam bath. Vanadium, iron, nickel, and ash determinations were made on the original and deasphalted oils. The results are given in Table II.

*Precipitation of Vanadium with the Asphaltenes of Common Solvents*

A residual fuel from Venezuela crude (80% vacuum reduced straight-run residuum and 20% cycle oil) was treated with six volumes of solvent per volume

TABLE II

PRECIPITATION OF VANADIUM, IRON, AND NICKEL WITH PENTANE ASPHALTENES

| | Fuel | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A, from Venezuela crude | | B, from Venezuela crude | | C, from Turner Valley crude | | D, from Redwater crude | | E, from Arabian crude | |
| | Orig. fuel | Deasph. oil | Orig. fuel | Deasph. oil | Orig. fuel | Deasph. oil | Orig. fuel | Deasph. oil | Orig. fuel | Deas ph oil |
| Composition | 100% therm. residue | | 60% residue + oils | | | | therm. residue + virgin crude | | 84% residue + cracked tars | |
| Pentane asphaltenes, % wt. | 8.4 | | 6.6 | | 8.1 | | 11.0 | | 9.8 | |
| Ash, % wt. | 0.05 | 0.01 | 0.05 | <0.005 | 0.01 | <0.005 | 0.02 | <0.005 | 0.035 | 0.01 |
| Vanadium, p.p.m. wt. | 108 | 13 | 84 | 4.3 | Nil | | 8.4 | 1.4 | 126 | 6.0 |
| Iron, p.p.m. wt. | 7.5 | 2.8 | 13 | 3.2 | 14 | 2.0 | 36 | 3.1 | 9.7 | 4.8 |
| Nickel, p.p.m. wt. | 19 | 2.1 | 5.3 | 1.5 | 4.2 | Trace | 0.6 | 1.6 | 7.3 | 1.2 |
| Reduction of vanadium conc., % | 88 | | 95 | | .. | | 83 | | 95 | |

of fuel at room temperature, using petroleum ether (b.p. 30-60°C.), naphtha (b.p. 75-120°C.), acetone, diethyl ether, *n*-pentane, and ethyl acetate. After standing overnight the asphaltene solids were collected on a filter and washed with fresh solvent. The filtrates were evaporated on a steam bath and finally under reduced pressure. Vanadium and ash determinations were made on the original fuel and on the deasphalted oils. The results are shown in Table III.

TABLE III

PRECIPITATION OF VANADIUM WITH THE ASPHALTENES OF COMMON SOLVENTS
FUEL:—135 p.p.m. VANADIUM, 0.055% ASH

| Solvent | Petroleum ether (30-60°C.) | Naphtha (75-120°C.) | Acetone | Diethyl ether | *n*-pentane | Ethyl acetate |
|---|---|---|---|---|---|---|
| Surface tension dynes, cm.$^{-1}$(25°C.) | 16.3 | 20.9 | 23.1 | 16.7 | 15.3 | 23.4 |
| Asphaltenes, % wt. | 12.5 | 3.3 | 56 | 5.0 | 12.8 | 13.7 |
| Ash in deasphalted oil, % wt.* | 0.009 | 0.033 | <0.005 | 0.02 | 0.009 | 0.008 |
| Vanadium in deasphalted oil, p.p.m. wt. | 19 | 133 | 25 | 69 | 22 | 15 |
| Reduction of vanadium conc., % | 86 | ≈Nil | 81 | 49 | 84 | 91 |

* *Filtration of diluted fuel oils generally removes about half of the ash forming substances such as silica and inorganic salts (1).*

*Analytical Methods*

For the metals in the ash, colorimetric methods modified by Snyder and Clark (10) were used with a Fisher Filter Electrophotometer. Vanadium was determined as phosphotungstovanadic acid using chloroform extraction of the 8-hydroxyquinoline complex and sodium carbonate fusion (13). Iron was determined as the ferrous complex of *o*-phenanthroline, using hydrated manganese dioxide precipitation to isolate iron and hydroxylamine hydrochloride for the reduction of ferric ion (8). Nickel was determined as nickelic dimethylglyoxime (9), the nickelous complex being oxidized with iodine solution. Ash was determined by A.S.T.M. Method D482-46.

## Results and Discussion

Precipitation of the asphaltenes with *n*-pentane removed similar amounts (83-95%) of the vanadium despite differing crude source, composition, and vanadium content of the original fuels. The major portion of the iron and nickel compounds were also removed with the pentane asphaltenes.

The amount of vanadium removed by the solvent (apart from the case of acetone) is approximately proportional to the asphaltenes precipitated; petroleum ether, ethyl acetate, and *n*-pentane removing similar amounts of vanadium. It will be seen that diethyl ether, despite a lower surface tension, precipitated considerably less vanadium and asphaltenes than did ethyl acetate. The naphtha fraction apparently removes asphaltenes of a molecular size higher than the vanadium compounds present in the fuel. Although acetone yielded a heavy precipitate, the deasphalted oil contained a considerable portion of the vanadium of the fuel. This may be due to the better solubility of the vanadium compounds in acetone.

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# HOLLOW CYLINDER METHOD OF MEASUREMENT OF $P^{32}$ IN PLANTS[1]

By A. M. Kristjanson, H. G. Dion, and J. W. T. Spinks

## Abstract

By compressing plant material containing radioactive phosphorus into the form of a hollow cylinder and placing around a thin-wall Geiger tube, a direct determination of $P^{32}$ can be made. A standard sample, made by mixing a definite quantity of the radioactive fertilizer with a definite quantity of inactive plant material of the same kind as that being analyzed, is the basis for the determination of fertilizer phosphorus uptake. For the same sample, the counting rate of a hollow cylinder of plant material is approximately 10 times that of a briquet.

## Introduction

Three distinctive methods of determining $P^{32}$ in plant material have been described. The first requires precipitation of phosphate in a pure chemical form (2, 4), the second the counting of $P^{32}$ in solution (1), and the third, the preparation of compressed briquets of plant material to be counted using an end-window counter (3).

This third method permits very rapid preparation and counting of samples of plant material. The amount of sample that can be counted is limited by the area of the counter window and the maximum range in plant material of $\beta$-particles from $P^{32}$ and is approximately three grams of material. Owing to biological dilution of $P^{32}$ in the growing plant and radioactive decay of $P^{32}$ during the growing season, a 3-gm. sample may give a prohibitively low count at the later stages of growth.

It occurred to the writers that, by placing a sample, in the form of a hollow cylinder, around a thin-wall Geiger tube, as shown in Fig. 1, a much larger sample could be counted than with a briquet under an end-window counter. A simple calculation indicated that the counting rate might be multiplied 10 times by this technique, thus materially extending the period of usefulness of this general method of counting.

Plant cylinders must have an equivalent thickness in excess of 500 mgm. per $cm.^2$, the maximum range in plant material of $\beta$-particles from $P^{32}$. Plant cylinders used in our experiments, with a linear wall thickness of 3/8 in., had an equivalent thickness from 800 to 1100 mgm. per $cm.^2$, varying somewhat with the type of plant material analyzed.

For a maximum count, the length of the sample cylinders must be at least equal to the length of the sensitive portion of the counting tube. Since the measurement of plant uptake of $P^{32}$ from radioactive phosphate fertilizers is

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*Contribution from the Departments of Soils and Chemistry, University of Saskatchewan, Saskatoon, Sask.*

based on a relative rate of counting compared to a standard sample, it is necessary to compare standard lengths of material compressed in a uniform way. By using a pressure 16,000 lb. per sq. in. for five minutes and having the cylinder length greater than the sensitive portion of the tube, the exact amount of material used for the cylinders was unimportant. Approximately seventy grams is necessary for the tube used in our work. If the amount of plant material available is less than this, shorter cylinders can be counted by putting a metal collar of the required height around the lower portion of the tube and counting shorter lengths of both standard and unknowns, which still must extend from the collar to beyond the upper limit of the sensitive portion.

*Design of Form and Preparation of Plant Sample*

A steel form was made to compress plant material into a hollow cylinder to use with a thin-wall counting tube available in this laboratory (Thyrode 1B85—length 8 cm., Victoreen Instrument Co., 5806 Hough Ave., Cleveland, Ohio). The steel form is illustrated in Fig. 2. It consists of a plunger which slides between an outer cylinder and a center post, both of which are joined to a base. The annular space is filled with dried, ground plant material, the plunger is inserted and the material pressed in a Carver laboratory press at 16,000 lb. per sq. in. for five minutes. The cylinder of plant material is removed by supporting the outer cylinder and center post from the bottom and applying further pressure to the plunger which pushes out the plant sample. The cylinder of plant material can then be lifted from around the center post by hand.

The plunger of the original form fitted very tightly and the first plant cylinders made were unsatisfactory as the lower portion was spongy and broke

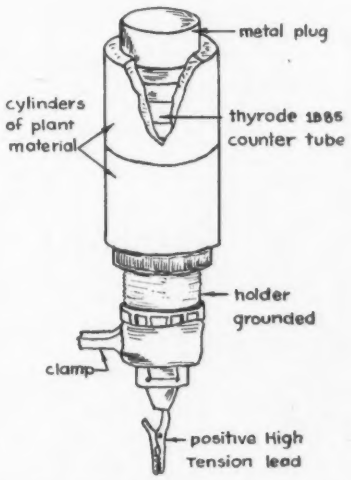


FIG. 1. *Hollow cylinder of compressed plant material around thin-wall Geiger tube.*

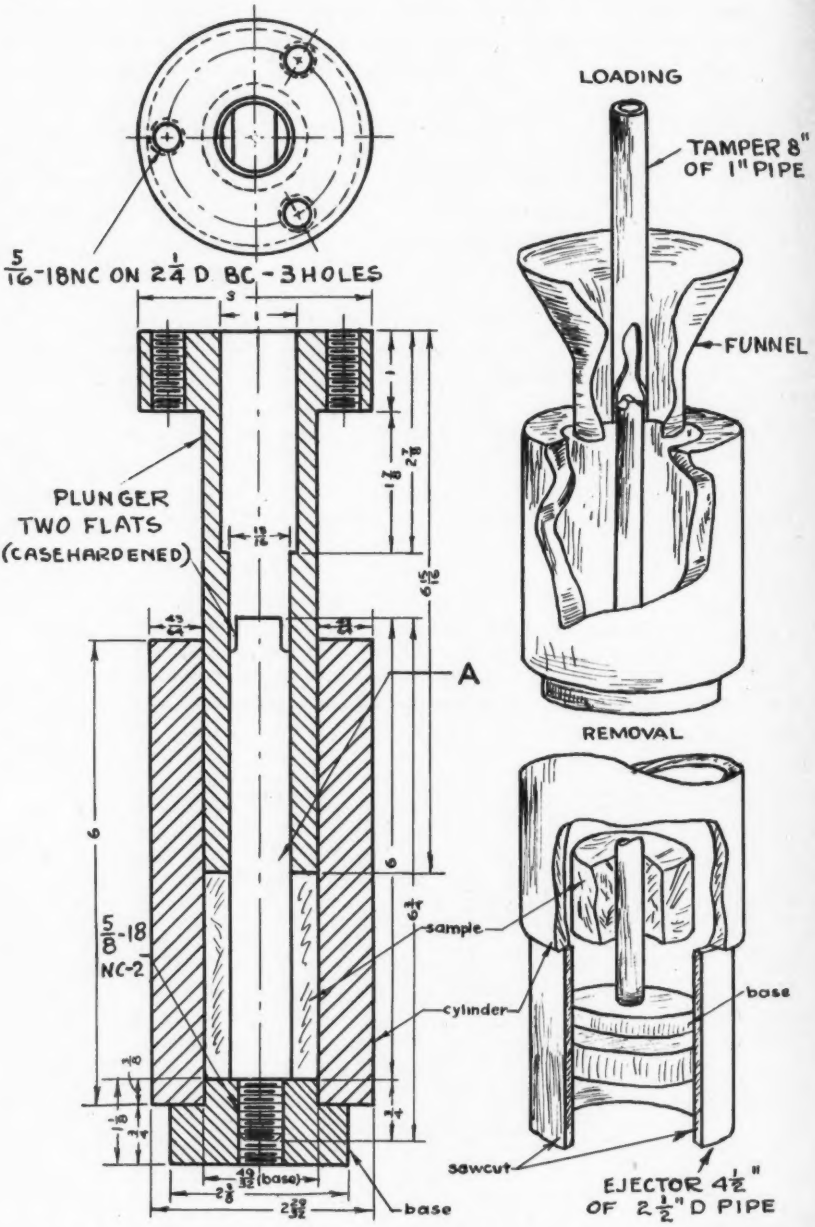


FIG. 2. *Steel form to compress plant material into a hollow cylinder. A = center post* $2\frac{5}{32}$ *D at base, taper .001" per inch.*

off on handling. This effect may have been due to trapped air as it was corrected by making the plunger fit less tightly.

To avoid using a steel form of unwieldy length the cylinders were made in half-lengths. The two halves fitted neatly together and counts on various pairs selected from four half cylinders made from one lot of active plant material showed the reproducibility of counting pairs of half cylinders to be adequate for this work. The average error in the activity of six combinations of half-cylinders, each sample counted for at least 10,000 counts, was 0.9%, the approximate error to be expected from statistical fluctuations in counting.

This method of determining $P^{32}$ in plant material has been used in our laboratory for green wheat plants, the grain of wheat, oats, and barley, for wheat straw and for a mixture of wheat straw and grain.

*Preparation of a Standard Sample*

A standard was prepared by mixing a known amount of radioactive fertilizer with a known weight of inactive plant material which was at the same stage

TABLE I

TESTS OF MIXING OF PREPARED STANDARDS

| Sample | | | Activity (c.p.m. × 1/64)* | % Relative error |
|---|---|---|---|---|
| Plant briquet | A | 1 | 40.7 | 0.25 |
| | | 2 | 40.8 | 0.49 |
| | | 3 | 40.8 | 0.49 |
| | | 4 | 40.2 | 0.99 |
| | | Mean | 40.6 | 0.56 |
| | B | 1 top | 93.2 | 0.75 |
| | | bottom | 93.9 | 0.00 |
| | | 2 top | 93.6 | 0.32 |
| | | bottom | 94.8 | 0.94 |
| | | Mean | 93.9 | 0.50 |
| | C | 1 top | 86.1 | 0.46 |
| | | bottom | 86.9 | 0.46 |
| | | Mean | 86.5 | 0.46 |
| Plant cylinder | D | 1 | 25.2 | 0.80 |
| | | 2 | 24.9 | 0.40 |
| | | 3 | 24.9 | 0.40 |
| | | 4 | 24.9 | 0.40 |
| | | Mean | 25.0 | 0.50 |
| | E | 1 | 9.87 | 0.30 |
| | | 2 | 9.77 | 0.71 |
| | | 3 | 9.89 | 0.51 |
| | | Mean | 9.84 | 0.51 |

* *c.p.m. = counts per minute.*

of growth and of the same kind as the samples to be analyzed. Powdered fertilizer can be thoroughly mixed with dry ground plant material by running the mixture through a grinder, then shaking on an end-over-end shaker for several hours.

Counts on replicate briquets or cylinders prepared from a large amount of active material, to check the thoroughness of mixing, are summarized in Table I. A count of 10,000-20,000 counts was obtained for each sample. Thus, the probable error due to statistical fluctuations in counting is approximately 0.5%. The reproducibility of the activity of replicate samples shows that complete mixing was achieved.

*Calculation of Fertilizer Phosphorus Uptake by Plants*

A standard sample, made by mixing a definite quantity of radioactive fertilizer with a definite quantity of inactive plant material of the same kind as that being analyzed, is the basis for the determination of fertilizer uptake. Since the amount of material counted in each cylinder is the same, the amount of a radioactive fertilizer taken up can be calculated by considering the relative weights and activities of samples and standard, thus:

$$\frac{\text{Wt. of sample}}{\text{Wt. of standard}} \times \frac{\text{activity of sample}}{\text{activity of standard}} \times \text{amount of fertilizer P in standard} = \text{amount of fertilizer phosphorus in sample.}$$

*Correction for Background Count*

The count of a cylinder of inactive plant material can be used to allow for background count on the field samples and on the standard. With a cylinder of inactive wheat grain the background count was approximately 60 counts per minute, which includes the count due to naturally occurring $K^{40}$ in plant material.

*Advantages of Counting as Cylinders*

For our experimental arrangement, the relative activity of a cylinder and a briquet is shown in Table II.

For $P^{32}$ this means that when the activity in briquets becomes too low to count accurately, the activity can be determined with the cylinder method

TABLE II

RELATIVE COUNTS OF CYLINDER AND BRIQUET

| Sample | Cylinder count (c.p.m. × 1/64)* | Briquet count (c.p.m. × 1/64) | Ratio $\frac{\text{cylinder count}}{\text{briquet count}}$ |
|---|---|---|---|
| 1 | 48.0 | 5.20 | 9.23 |
| 2 | 23.4 | 2.55 | 9.18 |
| | | | Mean 9.20 |

*c.p.m. = counts per minute.*

for approximately 40 days more or, alternatively, for investigations requiring the same time, one could use 1/10th the initial activity, counting cylinders rather than briquets.

By comparing unknown samples with the standard sample no correction for decay of $P^{32}$ is required, nor is precise counter control necessary. Providing the weight of active fertilizer in the standard is accurately known, a direct comparison gives the amount of active material in a sample of plant material. This comparison can be obtained with a count rate meter which is cheaper than more standard equipment. With this method, no lead shielding is needed, and the counting tubes employed are less expensive than end-window types.

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